THESIS PRESENTED by R.HAY, B.Sc., A.I.C., for the

DEGREE of Ph.D..

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The work has been carried out under the supervision of Professor J.H.Andrew,D.Sc., in the Metallurgical Laboratories of the Royal Technical College, Glasgow. In Book 1 are recorded the results of an investigation on the Roasting of Iron Pyrites together with the theoretical and practical deductions therefrom. In the same Book an account of experimental work upon the Constitution of Steel at Elevated Temperatures and its Influence upon Impact Brittleness is given.

Book 11 is largely devoted to a study of the Colloidal State in Metallic Systems, the Copper-Zinc Alloys and Duralumin being fully treated from this standpoint.

The Writer desires to place upon record his very deep gratitude to Professor Andrew for the great encouragement and kindly interest which he displayed in the work, and also for his many valuable suggestions and criticisms.

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Book 1.

Contents.

# SOME EXPERIMENTS UPON THE ROASTING OF IRON PYRITES.

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Although much work has been done upon the roasting of iron pyrites in large scale plant, chiefly in the manufacture of sulphuric acid, and, in a general way, the necessary conditions for good roasting in the various types of plant are known to practical men, yet very little systematic work has been carried out in this field. For this reason it was considered desirable to carry out a series of roasting experiments and, if possible, endeavour to follow the various stages in the roasting operation. Further it was deemed advisable to investigate the influence of the size of the particles and rate of the flow of the air through the furnace, upon the course of these reactions. For these purposes a study of the composition of the gases at various temperatures seemed the most promising method of investigation.

Before the work could be started much thought had to be given to the methods to be pursued and the apparatus to be used. One point of fundamental importance which had to be settled was, would the composition of the gas alter while the sample was being withdrawn from the furnace into the absorbing liquid on account of the alteration in the temperature. To decide this point a series of experiments was planned, the results of which showed that the gases could be withdrawn from the furnace without change of composition, provided glass tubing was used for the purpose and that no rubber came in contact with the gases.

## First series of Experiments.

Object:- To investigate if any $SO_3$ is formed when a mixture of $SO_2$ and air is passed through a Silica Tube when hot.

Apparatus:- This is shown in Figure 1. The tubes leading into the absorption bottles were drawn to a fine point, ground/

ground smooth, and adjusted, by means of a rubber joint on the tube, but well clear of the liquid, to touch the bottom of the bottle. By this means the gas stream was broken up into extremely fine bubbles about 1 m.m. in diameter and complete absorption was ensured. That the absorption was complete was proved by inserting a second wash bottle containing dilute solution of the absorbing reagent. This wash bottle always gave a blank result.

Procedure:- A mixture of air and $SO_2$ was passed through the silica tube which was inserted in an electrically-heated furnace. The air was supplied at the rate of a half litre per minute and $SO_2$ at three bubbles in two seconds. Samples of the emergent gases were drawn off through absorbents in the gas-wash bottles numbered 1 and 2, by means of aspirators. The volume of the sample was measured by the water run out into the measuring jars below. Suitable quantities of standard $\frac{N}{10}$ Potassium Iodide and Potassium hydroxide solutions were placed in the wash-bottles 1 and 2 respectively. A volume of about 500 ccs. was aspirated for each sample. The time required for each test was about 30 minutes so that a sample of about 3% of the gases was obtained. Starch was added to the Iodine solution and Phenolphthalin to the KOH solution and the gas was passed till the end points were reached; these could be determined very exactly and were arranged to come close together.

Tests were made first with the tube cold, and then the tube was heated to about 500° C. and another set of tests made. In each case the ratio of the volume of gas necessary to neutralise the KOH to that required to reduce the Iodine was determined thus:-

$$\text{Ratio} = \frac{\text{Reducing Power}}{\text{Acidity}} = \frac{\text{Ccs of gas to neutralise KOH}}{\text{Ccs of gas to reduce Iodine.}}$$

While the proportion "total acid" was constant, the reducing

power/

power decreased as the $SO_3$ content increased, so the fall of the ratio gave a measure of the $SO_3$ formed.

Results:- The following results were obtained. Presuming that there was no conversion in the cold tube, which is known to be the case, the heated tube shows considerable formation of $SO_3$. This was apparent from the volume of white fume emerging from the apparatus.

| Experiment. | Reduction. | | Acidity. | | Ratio = Reducing Power / Acidity. |
|---|---|---|---|---|---|
| | Ccs. Iodine. | Ccs. Gas. | Ccs KOH. | Ccs Gas. | |
| Tube Cold. | 25 | 585 | 10 | 480 | 0.821 |
| Tube Hot. | 25 | 655 | 10 | 510 | 0.778 |

Therefore $SO_3$ is formed when $SO_2$ and air are passed through a heated silica tube.

## Second Series of Experiments.

Object:- To investigate if any $SO_3$ is formed when a mixture of $SO_2$ and air is passed through a Heated Glass tube.

Apparatus:- The apparatus used was similar to that utilised for the previous set of experiments except that the silica tube was replaced by a hard-glass combustion tube.

Procedure:- A parallel set of tests to those carried out in the previous investigation was performed but as the experiment with the hot tube showed no conversion this was repeated several times in order to confirm this result.

Results:-

| Experiment. | Reduction. | | Acidity. | | Ratio = Reducing Power / Acidity |
|---|---|---|---|---|---|
| | Cos. $I_2$ | Ccs Gas. | Ccs KOH | Ccs Gas | |
| Tube Cold. | 25 | 815 | 10 | 660 | 0.810 |
| Tube Hot. | 25 | 700 | 10 | 570 | 0.814 |
| Tube Hot. | 25 | 640 | 10 | 525 | 0.820 |

In these experiments no white fumes were visible in the gases emerging from the furnace.

Summary:- The results for the cold Glass tube agree with those for the cold Silica tube, as would be expected. The results show that no change takes place in a heated Glass tube, so that an analysis of the gases drawn from a furnace by means of a Glass tube is representative of the gases in the furnace. This is supported by results derived from Contact sulphuric acid practice. In plant practice it was found that samples of ingoing and exit gases of the Converter Ovens when withdrawn through iron tubes gave "conversion" figures which were not in good agreement with the actual production figures of $SO_3$. The "conversion" figures were too low. When glass tubing was inserted inside the iron tube and samples withdrawn through the glass tubing higher conversion figures were obtained and these were in good agreement with the actual recovery figures. It was on the hot side, that is the exit side, that the greatest difference was observed. Some $SO_3$ was being decomposed in passing through the iron tube.

## Third Series of Experiments.

Object:- To investigate the stability of a mixture of $SO_2$, $SO_3$, and air when passed through a Glass tube which is maintained at different temperatures.

Apparatus:- The apparatus was slightly modified from that used in the previous experiments in that the $SO_2$ and air was passed over platinised magnesium sulphate in a furnace maintained at a temperature of 420°C. to obtain $SO_3$ in the gases. Moreover the $SO_2$ content only of the gas before and after passing through the heated Glass tube was determined in this case.

Procedure:- A mixture of $SO_2$ and air was passed into the first furnace which was a resistance furnace having a silica tube. In this tube was placed a porcelain boat into which was put 10 grams of platinised mass. This converted part

of/

of the $SO_2$ to $SO_3$.

A sample was drawn from the mixed emergent gases, through an absorption bottle containing N/10 iodine, by an aspirator, and the $SO_2$ content estimated. The gases then passed through a second furnace through which passed a Glass tube. A second sample was withdrawn from the gas stream as it emerged from this furnace and the $SO_2$ content determined as before. A series of experiments were carried out. The first set was carried out with the Furnace B cold, the second set with this furnace heated to about 600°C., the middle 12 inch portion of the 2 ft. 6 in. tube being heated, and the third set using the same temperature for the second furnace but heating the end of the tube nearest to the second absorption bottle. This meant that in one case the gases were cooled a little before passing into the absorbing medium and in the other case they were cooled only to a very slight degree. In order to further accentuate the second case the rate of aspiration was increased.

Results:-

| Experiment. | Before glass tube. | | After glass tube. | | Difference. |
|---|---|---|---|---|---|
| | Ccs. $I_2$. | Ccs. Gas. | Ccs. $I_2$. | Ccs. Gas. | |
| Tube Cold (B) | 25 | 1235 | 25 | 1275 | +2 |
| Tube Cold (B) | 25 | 540 | 25 | 550 | +2 |
| Tube Cold (B) | 25 | 520 | 25 | 524 | +1 |
| Tube Centre Hot | 25 | 448 | 25 | 453 | +1 |
| Tube Centre Hot | 25 | 440 | 25 | 438 | -0·05 |
| Tube End Hot | 25 | 720 | 25 | 713 | -1 |
| Tube End Hot | 25 | 895 | 25 | 908 | +1 |

Summary:- These results show that, within the limits of accuracy of the experiments, the gases $SO_2$, $SO_3$, and air do not alter in composition in passing through a heated Glass tube, but that in passing through a heated Silica tube, considerable change can take place.

It was found that when a deposit of carbon, from

decomposed corks, formed on the glass tube change of composition of the gas took place: this again is borne out by large scale practice. For this reason the glass tube was kept as clean and dry as possible.

The apparatus which was used for investigating the roasting of iron pyrites is shown in Figure 3. Having shown that the gases $SO_3$, $SO_2$ and $O_2$ can be withdrawn from the furnace through clean glass tubing without altering the state of equilibrium it was considered that the sequence of roasting reactions could best be studied by following the change in the $SO_2$ and $SO_3$ contents of the emergent gases. Knowing that the glass tube through which the gas samples is drawn must be clean the cork at the exit side of the furnace was replaced by a special carborundum joint. The air before passing into the furnace was dried by passing it through a calcium chloride drying tower. As a result of this precaution no acid condensed in the outlet tube.

Pressure gauges were fitted to the apparatus, one on the inlet side of the furnace and one on the aspirator. This ensured a constant pressure throughout the apparatus and also ensured that the pressure in the aspirator was the same in each test; thus increasing the accuracy of the results. The introduction of the nozzle on the inlet side allowed of more easy regulation of the rate of the air supply and by varying the size of the nozzle the amount of air passing was more easily and more accurately regulated. After some experimenting the best sizes of nozzles for the various rates of flow were obtained.

Another method of analysis was adopted. In order to minimise the number of volume readings, and so reduce liability to error, absorption in N/10 Iodine was adopted followed by another wash bottle containing N/100 Iodine. By adopting the precautions already mentioned in the earlier experiments/

experiments absorption was found to be complete in the 1st wash bottle. The $SO_2$ and $SO_3$ were absorbed in the same wash bottle. Also in these experiments only a certain amount of gas was drawn through the wash bottles, not sufficient to oxidise all of the Iodine. The excess of Iodine was determined by titrating with N/10 Sodium Thiosulphate and from this figure the amount of $SO_2$ in the known volume of the gas was calculated. An excess of thiosulphate was then added and the solution titrated to neutrality with N/10 NaOH and the amount of $SO_3$ in the known volume of the gas calculated. The method of calculation is as follows:- if x is the number of ccs. of N/10 NaOH and y equals the number of ccs of N/10 Iodine, then the weight of $SO_2$ equals 0.0032y grams and the weight of $SO_3$ equals 0.0040 (x - 2y) grams of $SO_3$. Taylor and Occleshaw found that this method gave very satisfactory results when checked against other methods of analysis but that it was desirable to titrate with thiosulphate immediately after the test was completed as a very slow oxidation of the $SO_2$ by $O_2$ takes place. This precaution was observed. Tests were carried out at intervals of 50°C. up to a maximum temperature of 900°C. The temperature of the furnace was measured by a thermocouple and the temperature was regulated by a rheostat. The oxygen content of the air was determined at frequent intervals by means of a Hempel gas apparatus. It was found to remain very constant throughout all the experiments, the figure obtained being 20.8%. It was essential that the oxygen content of the air remain constant.

The ore used in these roasting experiments was practically a pure iron pyrites. This ore was chosen so that the variables should be reduced to a minimum and so that more accurate deductions might be made from the data resulting from the experiments. Moreover no variation of composition would

be/

be obtained in the fine ore and the coarse ore; this point was confirmed by analysis. The analysis of the ore is given in the following table:-

| | I. | II. |
|---|---|---|
| Fe | 48.4 | 48.2 |
| S | 49.0 | 49.4 |
| Cu | 1.4 | 1.2 |
| $SiO_2$ | 0.8 | 0.76 |
| | 99.6 | 99.56 |

The ore was classified into various sizes and dried at 100°C. before being used in the various experiments.

10 grams of ore equivalent to 4.92 gms. of Sulphur were used for each experiment. The ore was placed in fireclay boat and it was rabbled at the end of each test.

For the first experiment the size of the ore used was through 20 mesh and lay on 50 mesh. The rate of flow of the air into the apparatus was kept constant throughout the experiment and was approximately 1/20 cubic foot per minute.

In Table I the data obtained during this experiment are set out and in Table II the calculated data, necessary for a study of the reactions involved in the roasting of the ore, are given. Fig.4. shows the information of Table II in graphical form.

From a study of Figure 4,it would appear that a series of reactions are involved and that each change in direction of the curves indicated some change in conditions.

The influence of the size of the ore, on the reactions involved, was next considered. To investigate this point three sizes of ore were selected. The sizes shown were 1/8", 10 mesh and 100 mesh. Throughout the various experiments the rate of flow of the air into the furnace was kept constant, the figure being the same as used in the earlier experiments./

experiment. The calculated data derived from these experiments are shown in Tables 3, 4 and 5, and the graphs drawn from the data are given in Figs. 5, 6 and 7. The general resemblance of these curves to Fig.4 is very striking, each curve being, as before, made up of a number of individual portions.

The other very important factor in roasting operations is the rate of supply of air to the furnace. This point was investigated by carrying out a series of experiments with varying rates of supply of air to the furnace, the size of the ore being maintained at a constant figure. For this purpose ore of 30 mesh size was used. The rate of flow of air was measured by the meter shown in Figure 3. The meter was also used to check the rates of flow in the earlier experiments so that a steady rate of flow might be attained. From preliminary experiments it was determined that using nozzles of $\frac{1}{2}$", $\frac{1}{4}$" and 1/32" diameter of pressure nozzle rates of flow of air of 1/10 cubic foot, 1/20 cubic foot and 1/30 cubic foot could be readily maintained over the whole period of the experiment. This device proved eminently more satisfactory than the earlier endeavours to control the rate of flow by means of screw clips. The air was supplied from a very large storage tank and the pressure of the air in the storage cylinder did not alter measurably during an experiment. A pressure gauge was fitted to the tank. The data obtained from these experiments are recorded in tables 6, 7, and 8 and shown in graphical form in Figures 8, 9 and 10. The curves show the same general features as those curves already mentioned. It may be mentioned in passing that in the two extreme cases of rapid flow of air and of finely comminuted ore the marked irregularities of the total curves is not nearly so pronounced. That these breaks, or changes in direction, of the curves are real, cannot/

cannot be doubted as they occur too persistently and too regularly to be explained away by experimental error.

The final product in the roasting of $FeS_2$ is $Fe_2O_3$ but $Fe_2(SO_4)_3$ is also formed during the operation if the temperature be too low. It is generally assumed that the reactions involved in "burning" of pyrites are represented by the equation

$$4FeS_2 + 11\ O_2 = 2Fe_2O_3 + 8SO_2$$

From a study of the heat balance of a Mannheim contact plant this equation would appear to meet the case in a general way. (See McNab[1] for figures). Some of the $SO_2$ would be oxidised to $SO_3$ so accounting for the small percentage of $SO_3$ found in the "burner" gases. However the reactions which take place during the roasting operation of $FeS_2$ must be very much more complex and it is the preponderance of one reaction over the others in certain ranges of temperature which must account for the various breaks in the curves.

Owing to the great experimental difficulties it is not possible to follow all the reactions taking place. But it is possible from theoretical reasoning to arrive at a fairly accurate account of the operation. For this purpose a study of the equilibrium constants with varying temperature is of great value. The van't Hoff Equation is the form generally used. This equation is

$$\frac{d \log K}{dt} = \frac{-Q}{RT^2}$$

To use this equation it is necessary to know one value of K for the reaction under consideration. This is necessary for in the integrated form of the equation a constant appears which it is not possible to evaluate.

By using the Nernst Heat Theorem the difficulty of the constant can, in a great measure, be overcome. In order to understand this theorem and to follow its application more/

[1] Technical Reports of Explosives Supply. 1921.

more clearly it will be advisable to show briefly its derivation.

For the van't Hoff isotherm for liquid or solid states the equation is of the form $A = RT \log K - RT \Sigma\nu \log C$

From the Clapeyron equation as applied to vapour pressure the value of log C can be determined

$$\Sigma\nu \log C = \frac{-\Sigma\nu\lambda_0}{RT} + \frac{\Sigma\nu\alpha_0 \log T}{R} + \frac{\Sigma\nu\beta_0 T}{R} + \cdots + \Sigma\nu\iota$$

where $\lambda_0$ = internal molar heat near 0° Absolute Temperature and internal molar heat of vaporisation $= \lambda_0 + \alpha T + \beta T^2 + \cdots$

$\iota$ = constant depending upon substance

$\Sigma\nu$ = algebraic sum of molecules taking part in the reaction i.e.

$\nu_1 A + \nu_2 B = \nu_1' C + \nu_2' D \qquad \Sigma\nu = \nu_1' + \nu_2' - \nu_1 - \nu_2$

From the fundamental equation of energy charge $A - Q = \left(\frac{dA}{dT}\right)T$ we get by a slight transformation the form $\frac{A}{T} = -\int \frac{Q}{T^2} dT$ + const.

$= a - \int \frac{Q}{T^2} dT$ where $a$ = a constant,

undeterminable by thermodynamics. The variation of Q with temperature can be expressed as $Q = Q_0 + \alpha T + \beta T^2 + \cdots$

where $Q_0$ = heat of reaction at Absolute Zero. Substituting this value of Q we get $\frac{A}{T} = a + \frac{Q_0}{T} - \alpha \log T - \beta T \cdots$ $\therefore A = Q_0 + aT - \alpha T \log T - \beta T^2 \cdots$

To calculate the constant "a", Nernst assumed that in the region of Absolute Zero $\frac{dA}{dT} = \frac{dQ}{dT} = 0$

so that we get $\frac{dA}{dT} = a - \alpha \log T - 2\beta T \cdots = 0$

and $\frac{dQ}{dT} = \alpha + 2\beta T + \cdots = 0$

from we get $a = 0$ and $\alpha = 0$

Hence $A = Q_0 - \beta T^2$

and similarly $Q_T = Q_0 + \beta T^2$

Therefore substituting the Nernst equation in the van't Hoff isochore above

$$RT \log K = -\Sigma\nu\lambda_0 + \Sigma\nu\alpha_0 T \log T + \Sigma\nu\beta_0 T^2 + \cdots Q_0 - \beta T^2 \cdots + \Sigma\nu\iota$$

$$= (Q_0 - \Sigma\nu\lambda_0) + \Sigma\nu\alpha T \log T - (\beta - \Sigma\nu\beta_0) T^2 \cdots + \Sigma\nu\iota$$

This equation may be regarded as an expression for a gaseous reaction carried out in the liquid or solid states.

Equating the constants of this equation with those of the usual isochore equation we get

$Q_{isochore} = (Q - \Sigma\nu\lambda_0)$

$-\alpha = \Sigma\nu\alpha$

$-\beta = \beta + \Sigma\nu\beta_0$

$Const = \Sigma\nu\iota$ = the summation of integration constants of vapour Pressure curve which can be determined by calculation.

Nernst further assumed $\alpha$ = 3.5 calories so that the equation now becomes $RT\log K_p = Q_0 + 3.5\nu T\log T - \beta T^2 \text{ ----- } + C$

$$\therefore \log_{10} K_p = \frac{Q_0}{4.57T} + 1.75\nu\log T - \frac{\beta T}{4.57} \text{ ----- } + C'$$

The values for the coefficients used above $\alpha, \beta$, etc. are readily obtained from the specific heat values of the reactants and products of any given reaction.

From Kirchoff's Law $\frac{dQ}{dT} = C_1 - C_2$ where $C_1$ = initial heat capacity of the system and $C_2$ = heat capacity of system after the reaction.

and $Q_T = Q_0 + \beta T^2$

$$\therefore \frac{dQ_T}{dT} = 2\beta T$$

For general purposes $\beta$ can be neglected as it is generally of a very small order. The errors in specific heat determinations and in heats of formation are generally more serious than the omission of $\beta$ etc. Also $Q_0$ can be taken as approx. equal to Q at ordinary temperature.

Therefore, as a first approximation, we may adopt the equation

$$\log_{10} K_p = \frac{Q}{4.57T} + 1.75\nu\log T + Const$$

Nernst has calculated the value of the constant for a large number of gases and for solids it can be neglected.

The variation of the value of the affinity value A is often useful as a guide to how a reaction will go with change of temperature.

As already shown $A = Q_0 - \beta T^2$

and the value of $\beta$ can be calculated from the specific heat values as previously stated.

As the value for the specific heat is not always available at/

at constant pressure it can be calculated from the constant volume figure and a modification of Grüneisen's equation.

Thus $C_p = C_v + C_p^2 \frac{T}{T_m} \times 0.0214$ where $T_m$ is the melting temperature.

The above theorem was applied to a number of possible equations which might possibly represent stages in the roasting of $FeS_2$ with a view to endeavouring to interpretate the experimentally derived curves.

There is a certain amount of practical evidence for assuming that on heating $FeS_2$ it is decomposed and S is liberated. Therefore the first reaction to be investigated will be $FeS_2 \rightleftharpoons FeS + S$.

Heat of formation of $FeS_2$ = 29150 calories.

" " " " FeS = 24000. " .

Sp.Ht. of $FeS_2$ = .1301 Molar Sp.Ht. at Const.Pressure = 120 x .1301 = 15.6

Sp.Ht. of FeS = .1357 " = 88 x .1357 = 11.94

" " " S = 0.18 " = 32 x 0.18 = 3.76

Q = - 5150 calories; $\therefore$ 15.6 - 15.7 = $2\beta$ T and for

T = 290 we get $= \frac{-.1}{580} = -.0002$

and $Q = Q_o + \beta T^2$

$\therefore -5150 = Q_o + (-0.0002T^2)$ $Q_o = -5150 + 0.0002T^2$

and $A = Q_o - \beta T^2$

$= (-5150 + 0.0002T^2) + 0.0002T^2$

$\therefore$ Affinity is negative but increases with temperature though even at 400°C the affinity from left to right is not appreciably reduced. But as the vapour pressure of the sulphur increases rapidly with increasing temperature, so sulphur will pass out of the system and to preserve equilibrium more $FeS_2$ will require to be decomposed. Hence this reaction is dependent entirely upon the vapour pressure of the sulphur. Actually it is the partial pressure of the sulphur which is the important item but for our purpose the relation between the vapour pressure of the sulphur and temperature will give a good indication of the reaction.

These values have been calculated and are given below in Table 9., and are also shown graphically in Fig.12.

Table 9.

| Temp. °C. | log.p. | p in m.m. |
|---|---|---|
| 0°C | -6.00 | $1.0 \times 10^{-6}$ |
| 100°c | -1.95 | $1.12 \times 10^{-2}$ |
| 200°C | + 0.18 | 1.51 |
| 300°C | 1.56 | 36.31 |
| 400°C | 2.54 | 346.7 |
| 444°C | 2.88 | 759.0 |

Under the conditions of the experiments the vapour pressure will not be quite as great but will rise in the same order. Therefore, at about 200°C, the partial pressure of sulphur will be quite appreciable and will rise very rapidly with increasing temperature.

The removal of the sulphur vapour from the system will be greatly assisted by the oxidation of the sulphur to sulphur dioxide according to the equation

$$S + O_2 \rightarrow SO_2 + 69260 \text{ calories}$$

$$C_p - C_p = 3.16 = 2\beta T$$

$$\beta = \frac{3.16}{2T} = \frac{1.58}{290} = .0054$$

i.e. $69260 = Q_o + 0.0054(290)^2$

$$Q_o = 69260 - 454 = 68806$$

$$\therefore \quad A = 68806 - 0.0058T^2$$

Molar heat of $O_2 = 6.96$

" " " $S = 6.09$

" " " $SO_2 = 9.89$

Therefore the affinity of the reaction is positive but decreases with increasing temperature.

Also $\log K_p = \frac{69260}{4.57T} - 1.75 \log T - 2.5$ taking the values for the constants

$O_2 = 2.8$

$SO_2 = 3.3$

S vapour $= 3.0$

and as $K_p = \frac{p_{SO_2}}{p_S + p_{O_2}}$

therefore/

therefore, with increasing temperature, which results in $\log K_p$ becoming less, the partial pressure of the $SO_2$ will become less resulting in the less rapid removal of the sulphur vapour from the system. Calculating $K_p$ for 900°C the value obtained is $K_p = 1{\cdot}12 \times 10^5$ This means that even at 900°C the amount of $SO_2$ is very high; in fact it must be practically 100% assuming, of course, only $SO_2$, $O_2$ and S present.

Thus if $x$ = *partial pressure of* $SO_2$

then $\frac{1-x}{2}$ = *partial pressure of* $O_2$

$\frac{1-x}{2}$ = *partial pressure of S vapour*

$\therefore \frac{x}{(\frac{1-x}{2})^2} = 1{\cdot}12 \times 10^5 \quad \therefore x \doteq 1$

This means that whenever the sulphur is liberated from the $FeS_2$ it will be rapidly oxidised to $SO_2$ when the temperature is such that the velocity of reaction is high.

FeS which results from the decomposition of the $FeS_2$ will be oxidised to $Fe_2O_3$.

The equation representing the reaction may be as follows:-

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2 + 472240 \text{ calories}$$

$\therefore 2\beta T = (4\times11{\cdot}94 + 7\times6{\cdot}96) - (2\times23{\cdot}30 + 4\times9{\cdot}89)$

$= 10{\cdot}32$

Molar heat $FeS = 11{\cdot}94$
" " $Fe_2O_3 = 23{\cdot}30$
" " $O_2 = 6{\cdot}96$
" " $SO_2 = 9{\cdot}89$

$$\beta = \frac{5{\cdot}16}{T} = 0{\cdot}0178$$

$$Q = Q_0 + {\cdot}0178T^2$$

$$472{,}240 = Q_0 + {\cdot}0178 \times 292^2$$

$$\therefore Q_0 = 472{,}240 - 1497 = 470743$$

$$A = Q_0 - {\cdot}0178T^2$$

$$= 470{,}743 - 0178T^2$$

$\therefore$ the affinity of the reaction is very positive but falls off with increasing temperature though at 900°C it is still very large, namely A = 446,250.

Also $\log K_p = \frac{470743}{4{\cdot}57T} - 3\times1{\cdot}75\log T - 6{\cdot}8 = \frac{(p_{SO_2})^4}{(p_{O_2})^7} = \frac{x^4}{(1-x)^7}$

where $x$ = partial press. of $SO_2$
$1-x$ = partial press. of $O_2$

For $T = 900°C = 1173°A.T.$

$\log K_p = 70{\cdot}86 \quad \therefore K_p = 9{\cdot}4\times10^{70} = \frac{x^4}{(1-x)^7} \quad \therefore x \doteq 1$

Consequently even at 900°C the reaction will proceed rapidly to the right. At low temperature it will also go in the same direction with equally great tendency but the velocity of the reaction will drop off at very low temperatures.
The sulphur dioxide formed by the oxidisation of the sulphur and the FeS will, in turn, be oxidised to sulphur trioxide. This reaction, unlike the preceding ones, is greatly affected by the presence of certain substances which act as accelerators or catalysts. The reaction itself is slow, that is, the rate of reaction is slow but this is considerably altered by certain substances. Platinum is the most efficient catalyst as its optimum temperature for rapid "conversion" of the $SO_2$ to $SO_3$ is at a temperature at which $SO_3$ is stable in the presence of $O_2$. $Fe_2O_3$ is also a catalyst, in that it accelerates the formation of $SO_3$ but unlike Platinum it also combines with the $SO_3$ to form ferric sulphate so that to get the maximum yield of $SO_3$ we must have a temperature at which ferric sulphate is slightly dissociated. All that is necessary is that the $SO_3$ pressure of dissociation be the same as that of the $SO_3$ partial pressure in the gases. Unfortunately from an efficiency point of view this temperature lies above the range of maximum stability of $SO_3$.

Using the first approximation of the Nernst Heat Theorem the variation of the equilibrium constant with temperature can be obtained & from this the degree of dissociation of $SO_3$ at various temperatures can be calculated.

The equation of the reaction is $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45{,}280$ calories.
Taking $Q_0 = 44{,}610$ calories and using this first in the Nernst Equation we have $\log_{10} K_p = \frac{44610}{4.57T} - 1.75 \log T - 2.4$

$$\text{also } K_p = \frac{P^2_{SO_3}}{P^2_{SO_2} \cdot P_{O_2}}$$

Now let x = degree of dissociation of $SO_3$

then 1 - x = amount of $SO_3$, and x = amount of $SO_2$ and $\frac{x}{2}$ = amount of $O_2$.

From this $p_{SO_3} = \frac{1-x}{1-x+x+\frac{x}{2}} = \frac{1-x}{1+\frac{x}{2}}$

$$p_{SO_2} = \frac{x}{1+\frac{x}{2}}$$

$$p_{O_2} = \frac{x}{2} \times \frac{1}{1+\frac{x}{2}} = \frac{x}{2\left(1+\frac{x}{2}\right)}$$

$$\therefore K_p = \frac{(1-x)^2}{\left(1+\frac{x}{2}\right)^2} \times \frac{\left(1+\frac{x}{2}\right)^2}{x^2} \times \frac{2\left(1+\frac{x}{2}\right)}{x}$$

$$= \frac{(1-2x+x)\left(1+\frac{x}{2}\right)2}{x^3} = \frac{2-3x+x^3}{x^3}$$

i.e. $K_p = 1 - \frac{3}{x^1} + \frac{2}{x^3}$

∴ when $K_p$ is very large the first two terms can be neglected and we have $K_p \fallingdotseq \frac{2}{x^3}$ so that dissociation is negligible. From the following table it will be seen that under 400°C, $K_p$ is very large and consequently at temperatures below 400°C dissociation of $SO_3$ is negligible.

The results obtained from the above equations are set out in Table 10 and graphically in Figure 12.

Table 10.

| Temp °C. | Temp. °Absolute. | $\log_{10} K_p$. | $K_p$ | Percentage dissociation of $SO_3$ |
|---|---|---|---|---|
| 0 | 273 | 29.14 | $1.38 \times 10^{29}$ | negligible. |
| 100 | 373 | 19.27 | $1.86 \times 10^{19}$ | " |
| 200 | 473 | 13.55 | $3.55 \times 10^{13}$ | " |
| 300 | 573 | 9.81 | $6.46 \times 10^{9}$ | " |
| 400 | 673 | 7.16 | $1.45 \times 10^{7}$ | 0.2% |
| 500 | 773 | 5.62 | $4.17 \times 10^{5}$ | 1.0% |
| 600 | 873 | 3.64 | $4.32 \times 10^{3}$ | 8.0% |
| 700 | 973 | 2.40 | $2.53 \times 10^{2}$ | 18.0% |
| 800 | 1073 | 1.29 | $1.97 \times 10^{1}$ | 36.0% |
| 900 | 1173 | 0.5508 | 3.55 | 56% |

The only remaining reaction which which need receive any special consideration is that of the decomposition of $Fe_2(SO_4)_3$. This reaction takes place according to the equation

$$Fe_2O_3 + 3SO_3 \rightleftharpoons Fe_2(SO_4)_3 + 128{,}700 \text{ calories.}$$

The percentage decomposition of ferric sulphate or the pressure of the $SO_3$ formed at various temperatures can be calculated from the Nernst equation. For the decomposition of the sulphate the value of $\log_{10} K_p$ is given by the following equation

$$\log_{10} K_p = \frac{-128700}{4.57T} + 3 \times 1.75 \log. T + 3 \times 3.5$$
$$= 3 \log. P_{SO_3}$$

In Table 11 are given the results of $K_p$ obtained for different values of T. From these values the pressure and also the percentage decomposition have been computed and are also given in the table below:-

Table 11.

| Temp °C. | Temp. °A.T. | $\log_{10} K_p$ | log $P_{SO_3}$ | $P_{SO_3}$ | p. in m.m. | % decomposition. |
|---|---|---|---|---|---|---|
| 600 | 873 | -8.62 | $\bar{3}.11$ | 0.0013 | 1.0 | .13 |
| 650 | 923 | -4.44 | $\bar{2}.52$ | 0.033 | 25.2 | 3.3 |
| 700 | 973 | -2.759 | $\bar{1}.08$ | 0.120 | 91.2 | 12.0 |
| 750 | 1023 | -1.317 | $\bar{1}.561$ | 0.364 | 276.0 | 36.4 |
| 800 | 1073 | +0.30 | 0.010 | ≒1.00 | ≒760.0 | ≒100 |

At temperatures in the neighbourhood of 600°C the vapour pressure of $SO_3$ from the dissociation of the ferric sulphate is appreciable so that at a temperature of approximately 550°C it will begin to decompose. At temperatures below this latter figure ferric sulphate will be formed by the interaction of $Fe_2O_3$ and $SO_3$, so that at temperatures below 550°C the yield of $SO_3$ will be poor.

The curve for the dissociation of Ferric sulphate in relationship to temperature variation is given in Figure 13.

On Figure 14 the curves which have been arrived at theoretically are all plotted together having the temperature axis common to all. This curve shows the fundamental changes which/

which ~~took~~ take place upon heating $FeS_2$ and that these changes have a real practical bearing is borne out by the curves obtained from the experimental results.

Whilst these theoretical curves permit of a very satisfactory qualitative examination of the experimental curves being made, it is, nevertheless, not possible to derive quantitative data from them. These curves give the equilibrium conditions as temperature varies but say nothing on the very important subject of the rate of the reactions at the varying temperatures. For example in the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ the conditions for $SO_3$ formation are very suitable at low temperatures according to the data arrived at, yet it is well known in practice that at temperatures below 300°C very little $SO_3$ is formed even under the best conditions. Moreover even at 400°C the amount of $SO_3$ would be small if an accelerator, such as Pt-black, were not adopted in practice.

The probable curves for $SO_2$ and $SO_3$ have been drawn in Fig.14 from a consideration of the calculated data. For the $SO_2$ curve the portion AB will follow in a general way the dissociation curve for $FeS_2$. Assuming that the FeS readily oxidised to $SO_2$ - the rate of this reaction will increase with temperature, so that slope of curve will be greater than shown - and that no secondary reactionsoccur this curve would continue as a smooth curve until the system contained only $SO_2$ and $Fe_2O_3$. However at a temperature around 350°C the $SO_2$ curve will change direction and the quantity of $SO_2$ being formed will cease to increase. This is due to the oxidation of $SO_2$ to $SO_3$. Over the portion of the curve BC, $SO_3$ will be formed in large quantity. But at C the curve will commence to rise again due to the fact that about 450°C the stability of $SO_3$ begins to decrease in a marked manner and as the temperature increases the rate of formation of $SO_3$ decreases faster and faster. Consequently over the portion of the curve CD, the $SO_2$ content increases, because the $SO_2$ from the oxidation of the FeS will become more and more/

more stable with increasing temperature. The exact temperature at which all the $FeS_2$ will be oxidised to $Fe_2O_3$ and oxides of sulphur is difficult to fix, but it will be in the neighbourhood of 550°C. This temperature will vary with the size of the pyrites pieces but, in the limit, will approach this figure. This is borne out in the experimental curves and is further substantiated by practice, in that, in sulphatising roasting of copper ores, the maximum optimum temperature is found to be about 650°C, this latter temperature being high enough to obtain a large amount of the iron in the state of $Fe_2O_3$; that is, it has all been converted to sulphate and then decomposed. In the theoretical case - if 550°C be the temperature at which all $FeS_2$ is oxidised - there will be a slight drop in the curve as shown in portion DE. At E the curve will again commence to rise but not so steeply as formerly. This increase in the $SO_2$ content comes from the decomposition of the ferric sulphate. At 600°C this decomposition is just becoming appreciable and the $SO_3$ formed will, to a very large extent, be decomposed giving rise to $SO_2$. Theoretically at a temperature of 800°C ferric sulphate will completely decompose so that above this temperature the $SO_2$ content should rapidly fall off. The exact temperature of the beginning of this fall and at which there will be no $SO_2$ present will vary with the size of the particles. Further as it is not pure oxygen but air which is used in the experiments, and also in practice, this point will be further modified by the partial pressure of the nitrogen. The portion of the curve EFG shows the change due to the decomposition of the ferric sulphate. The theoretical curve for the $SO_3$ content of the gases can be similarly arrived at. At temperatures below 300°C there will be practically no $SO_3$ in the system. At this temperature $SO_3$ will begin to be formed and will increase in amount at an

increasing/

increasing rate as the temperature approaches 400°C. But as the $SO_3$ is increasing so also is the amount of $Fe_2O_3$ in the system increasing. The $Fe_2O_3$ combines with the $SO_3$ to form $Fe_2(SO_4)_3$ but exactly at what temperature this reaction begins to be really important, it is difficult to say. It is safe to say that at 400°C the rate of reaction is becoming quite appreciable so that from about this temperature up to a temperature of 600°C, at which temperature the dissociation of ferric sulphate sets in, there is practically no increase of the $SO_3$ content of the system. Practically all the $SO_3$ which if formed goes into combination with the $Fe_2O_3$. The portion of the $SO_3$ curve, marked OP, shows the increase in $SO_3$ and that marked PQ, the range over which the $SO_3$ is going to ferric sulphate. At Q, the $SO_3$ content increases due to the dissociation of the sulphate. This amount will increase with temperature as the rate of dissociation with increasing temperature is greater than the rate of dissociation of the trioxide of sulphur. At about 800°C the amount of $SO_3$ in the system should commence to follow off but, as explained previously, the exact location of this point of decrease in $SO_3$, is difficult to fix precisely.

A comparison of the actual curves obtained by experiment with the curves on Fig.15 is of interest. In Figure 4 an average type of curve is depicted. The conditions were the rate of air supply, about 1/20 cubic feet of air per minute and the ore size, 20-50 mesh. Unfortunately in this series of experiments 400°C was the lowest temperature at which tests were made. The $SO_2$ curveshows a flat portion from B to C between the temperatures 400°C and 500°C. This corresponds with the range of $SO_3$ formation. At C the curve rises rapidly to D at 550°C. There is no fall from D to E but the curve is practically flat. From E at 600°C to F at 800°C the curve rises fairly steeply and at E it falls/

falls again. The curve for $SO_3$ also conforms tothe deduced curve in that it remains flat from 400°C to 600°C showing that the $SO_3$ formed is going to ferric sulphate formation. At 600°C the slope of the curve gradually increases becoming greater with increasing temperature. There is no decrease in the rate of $SO_3$ formation up to 900°C indicating that the amount of ferric sulphate undergoing dissociation is still sufficiently great to cause an increase of the $SO_3$ content, although not sufficient to maintain the high percentage of the $SO_2$ content.

The effect of the size of the ore particles upon the roasting is shown in Figs.5, 6, and 7. In the experiments upon which these curves are based the rate of flow of air into the apparatus was kept constant. In Fig.5 the results for pieces of ore 1/8" in size are given. The $SO_2$ curve again follows the general type but as the size of the particles is relatively large, roasting would not take place uniformly throughout the pieces. Therefore, as would be expected, the changes are not so marked as equilibrium conditions are not strictly maintained. The portion BC is not so flat as in the previous case and the point C is not clearly marked. Also the point D at 500°C - the point of completion of roasting - is also indistinctly marked whilst at F the curve does not fall but simply changes its direction, rising more slowly. The $SO_3$ curve continues along the zero line to 400°C showing that the little $SO_3$ which has been formed from B to C has been sufficient only to satisfy the sulphate formation reaction. Between 400°C and 450°C more $SO_3$ than is required by the former reaction is available and so free $SO_3$ appears in the system. From P to Q that is from 450°C to 650°C the $SO_3$ concentration remains constant but at 650°C it begins to increase and increases with rising temperature due to the dissociation of/

of the Ferric sulphate.

In Figure 6, the results of experiments carried out on ore of 10 mesh are recorded. In this case equilibrium conditions appear to be much more closely approached. The $SO_2$ curve shows all the characteristic portions. AB is due to $SO_2$ formation and increases with temperature. At B the curve rounds into the flat part BC from 350°C to 450°C which is the range of oxidation of $SO_2$ to $SO_3$. At D 550°C, after the rapid rise CD the curve changes its slope and the rate of $SO_2$ formation being much less rapid and arising from the decomposition of the Ferric sulphate. At 800°C the curve ceases to rise, gradually falling away. The $SO_3$ curve starts at 250°C and rises more gradually up to the point P at 400°C thus indicating the gradually increasing $SO_3$ content of the system, the amount being more than required for sulphate formation between 250°C and 400°C. From 400°C to 550°C the curve is similar to those derived from the previous experiments. At 550°C the curve commences to rise this being lower than in the earlier experiments but nevertheless in good agreement with the theoretical curve. Moreover at 800°C the slope of the curve becomes less, indicating a falling-off of the $SO_3$ formation, arising from the dissociation of the sulphate and is thus more in accordance with complete equilibrium.

Figure 7 shows the results in graphical form for ore of 100 mesh. In this case, due to the fine state of division of the ore equilibrium conditions were very closely approached. The changes of direction in the curves are much more gradual as would be expected in true equilibrium conditions. For the $SO_2$ curve the slope is steep over the range of temperature from 150°C to 250°C but after 250°C it gradually becomes less/

less steep as the amount of $SO_2$ converted to $SO_3$ increases. This continues up to a temperature of 400°C after which the amount of $SO_2$ in the system again increases as the optimum temperature of $SO_3$ formation is passed. At 500°C the rate of $SO_2$ formation falls off because, as previously assumed, all the pyrites is oxidised. From 500°C to 750°C the amount of $SO_2$ goes on increasing but not at the same rate as from 400°C to 500°C. From 800°C the concentration of the $SO_2$ in the system gradually falls off decreasing rapidly with increasing temperature. Similarly the $SO_3$ curve follows equilibrium conditions very closely. The formation of $SO_3$ begins to show at about 250°C and gradually increases with temperature. From 400°C to 500°C the rate of $SO_3$ formation just keeps pace with the rate of ferric sulphate formation but at 550° C the sulphate begins to dissociate and the curve of the $SO_3$ concentration gradually increases and becomes steeper with increasing temperature. At 800°C. the curve shows a sudden change of direction and the $SO_3$ in the system ceases to increase. This is what was expected from the calculated data. In this curve, therefore, the size of ore and rate of flow of the gases are practically correct to give equilibrium conditions.

In Figures 8, 9 and 10 the effect of varying the rate of flow of gases through the system, whilst the size of ore was kept constant, is shown. In Figure 8 the air was passed into the system at the rate of 1/10 cubic foot per minute, the size of the ore being 30 mesh. The $SO_2$ curve is practically one smooth curve from the start at 300°C to 700°C. Then from 800°C upwards the curve falls again. The $SO_3$ curve also shows a different type of curve rising continuously from 300°C to 550°C, changing direction and rising again to 800°C, at which point/

point there is another point of inflection in the curve. It is to be noted that the concentration of $SO_2$ was very low at the lower temperatures, whilst the concentration of $SO_3$ increased over a much larger range of temperature. The gas concentrations were favourable for a large amount of conversion of the $SO_2$ to $SO_3$ at the optimum temperatures. But while the conditions were good for the gaseous reaction the speed of the gases appears to have been too high to allow of the best conditions being established between the solid and gaseous states. This is also noticeable at 800°C for whilst the $SO_2$ is falling rapidly, the $SO_3$ is still rising quite rapidly in concentration. This means that dissociation was still quite active above 800°C and that equilibrium was not established but the rate of dissociation was not fast enough to keep up to $SO_2$ concentration of the gases.

In Figure 9 with the gas passing at 1/20 of a cubic foot per minute, the curve returns to the more general form. For the $SO_2$ curve the form is similar to that already discussed with the exception of a marked break at 650°C in the direction of the curve. It is difficult to account for this break and also the one at 550°C. As the 550°C has persisted throughout all the curves, it seems well established. The break at 650°C would appear to be connected with the dissociation of the ferric sulphate in this case. It may be that the 650°C marks the end of the pyrites oxidation in this particular case and that the 550°C point may be due to some slight experimental error. With this exception the curve is normal. The $SO_3$ curve is quite typical of the earlier cases.

The results of increasing the rate of flow of air into the apparatus are shown in Figure 10. The $SO_2$ curve is again in good agreement with the previous experiments. The 550°C is very clearly marked in this series of experiments.

The/

The decrease in the $SO_2$ concentration from 550°C to 600°C and the sharp change in the curve at the latter temperature due to the $SO_2$ coming from the dissociation of the sulphate point to the fact that in this region the oxidation of the pyrites completed itself. The $SO_3$ concentration curve is normal. The rate of flow seemed to allow of equilibrium in the heterogeneous system of gas and solid being approximated to.

In Figures 15 and 16 are shown the variation of the percentage conversion of $SO_2$ to $SO_3$ in the gases for the different sizes of ore and the different rates of flow of gases in the system respectively. It is to be noted that whilst the size of the ore did not affect the maximum percentage conversion to an appreciable extent, yet with the finer particles of ore conversion took place at a much lower temperature. On the other hand the concentration of the air affects the amount of conversion very appreciably. For high concentration of air very much better conversion is possible. This is what theory would lead us to anticipate for, from the law of Mass Action, the greater the partial pressure of the oxygen, the greater will be the amount of $SO_3$ formed. By writing the ordinary equation in the form $\frac{PSO_3}{PSO_2} = K\sqrt{PO_2}$, this is readily observed.

In the Mannheim Contact Plant the oxide shaft which carries the iron oxide catalyst is situated adjacent to the pyrites burners. It is packed to a depth of about 7' 6" with approximately 2" lumps of $Fe_2O_3$ ("burnt ore"). To obtain the best results in the oxide shaft, running with as high an oxygen content as possible would form the best practice.. Actual variations of gas concentration on conversion in the oxide shaft have not been studied in practice. In ordinary practice all air is drawn through the/

the burners so that it is not feasible to run with too high an $O_2$ concentration. In general practice the $SO_2$ content of the burner gas is about 6 to 7%. This point is worthy of investigation as in good practice about 33% is the amount of conversion obtainable. It might be possible to obtain considerably over 40% with correct concentrations of $SO_2$ and $O_2$.

Another very important point which is brought out in the foregoing experiments is the importance of temperature in the formation and dissociation of ferric sulphate. That the function of the iron oxide is not truly chemical in its nature has been shown by the work of Keppeler and D'Ans (Zeit Angew. Chem. 1908. 21 and Zeit physik Chem. 1908, 62.). Their work undoubtedly shows that the trioxide $SO_3$ is first formed and then combines with the oxide of iron, so that the physical state of the surface is of great importance. Nevertheless the temperature conditions must be correct for the formation and dissociation of the ferric sulphate. Theoretically what is necessary is, that the partial pressure of the $SO_3$ in the gas is equal to the dissociation tension of the ferric sulphate. If the temperature fall below that required to give the correct dissociation pressure of the $SO_3$, then the gas will be absorbed by the ferric oxide to form ferric sulphate. Moreover, as is seen from the curves, if the $SO_2$ concentration is increased, a higher temperature is required to bring about a corresponding amount of ferric sulphate dissociation (Compare Figures 5 and 7; the variation in the size of particles could not alter the temperature of dissociation of ferric sulphate). This point of temperature control of the oxide shaft does not receive enough attention in practice. In practice I found that a temperature of 620°C in the middle of the oxide shaft gave better results than one of 590°C on a 6 to 7% $SO_2$/

$SO_2$ content of burner gas.

No light is shed upon the question of whether increased surface will increase the percentage conversion. It is probable that the physical state of the surface is of much more importance than mere area of surface, as is the case with the platinum contact.

Where sulphatising roasting is the object in view, then the temperature must not exceed 600°C if ferric sulphate is wanted. But if the iron is desired in the state of oxide as is the case in certain sulphatising roasting operations, then a temperature in excessof this figure is required.

Table I.

| Temp. °C. | Vol. of N/10 $Na_2S_2O_3$ ccs. | Wt. of $SO_2$ gms. | Vol. of $SO_2$ ccs. | Vol. of N/10 NaOH ccs. | Wt. of $SO_3$ gms. | Vol. of $SO_3$ ccs. |
|---|---|---|---|---|---|---|
| 400 | 25.3 | 0.079 | 27.6 | 56.8 | 0.030 | 8.40 |
| 450 | 25.0 | 0.080 | 27.9 | 57.5 | 0.030 | 8.40 |
| 500 | 24.8 | 0.081 | 28.3 | 57.4 | 0.031 | 8.65 |
| 550 | 20.0 | 0.096 | 33.5 | 67.8 | 0.031 | 8.65 |
| 600 | 19.8 | 0.097 | 33.9 | 68.4 | 0.032 | 8.93 |
| 650 | 17.2 | 0.105 | 36.7 | 73.6 | 0.032 | 8.93 |
| 700 | 16.4 | 0.107 | 37.4 | 75.2 | 0.032 | 8.93 |
| 750 | 15.0 | 0.112 | 39.2 | 78.3 | 0.033 | 9.20 |
| 800 | 10.3 | 0.127 | 44.8 | 90.0 | 0.043 | 12.00 |
| 850 | 11.7 | 0.123 | 43.0 | 88.9 | 0.049 | 13.60 |
| 900 | 11.7 | 0.123 | 43.0 | 89.7 | 0.061 | 16.75 |

TABLE II.

| Vol.of gas aspirated. ccs. | Vol. of $SO_2$ ccs. | Vol.of $SO_3$ ccs. | % $SO_2$ | % $SO_3$ | % Conversion of $SO_2$ to $SO_3$. | Temperature of furnace. $^oC.$ |
|---|---|---|---|---|---|---|
| 500 | 27.6 | 8.40 | 5.15 | 1.56 | 23.4 | 400 |
| 500 | 27.9 | 8.40 | 5.20 | 1.56 | 23.2 | 450 |
| 500 | 28.3 | 8.65 | 5.27 | 1.60 | 23.4 | 500 |
| 500 | 33.5 | 8.65 | 6.18 | 1.59 | 20.5 | 550 |
| 500 | 33.9 | 8.93 | 6.24 | 1.64 | 20.8 | 600 |
| 500 | 36.7 | 8.93 | 6.74 | 1.64 | 19.6 | 650 |
| 500 | 37.4 | 8.93 | 6.85 | 1.63 | 19.3 | 700 |
| 500 | 39.2 | 9.20 | 7.15 | 1.68 | 19.0 | 750 |
| 500 | 44.8 | 12.00 | 8.05 | 2.16 | 21.2 | 800 |
| 500 | 43.0 | 13.60 | 7.74 | 2.45 | 24.0 | 850 |
| 500 | 43.0 | 16.75 | 7.70 | 3.00 | 28.1 | 900 |

TABLE III.

| Vol.of gas aspirated ccs. | Vol.of $SO_2$ ccs. | Vol.of $SO_3$ ccs. | $\%SO_2$ | $\%SO_3$ | %Conversion $SO_2$ to $SO_3$ | Temp. of furnace. °C. |
|---|---|---|---|---|---|---|
| 500 | 14.3 | Trace | 2.79 | - | - | 150 |
| 500 | 15.7 | Trace | 3.14 | - | - | 200 |
| 500 | 18.5 | Trace | 3.70 | - | - | 250 |
| 500 | 19.1 | Trace | 3.82 | - | - | 300 |
| 500 | 19.7 | Trace | 3.94 | - | - | 350 |
| 500 | 20.6 | Trace | 4.12 | - | - | 400 |
| 500 | 23.2 | 6.1 | 4.80 | 1.13 | 21 | 450 |
| 500 | 25.8 | 6.2 | 4.85 | 1.17 | 19.4 | 500 |
| 500 | 26.0 | 6.2 | 4.90 | 1.17 | 19.3 | 550 |
| 500 | 29.75 | 6.2 | 5.32 | 1.16 | 17.3 | 600 |
| 500 | 32.3 | 6.1 | 6.00 | 1.13 | 15.9 | 650 |
| 500 | 33.1 | 6.5 | 6.15 | 1.20 | 16.4 | 700 |
| 500 | 38.7 | 9.3 | 7.06 | 1.70 | 19.4 | 750 |
| 500 | 41.4 | 9.9 | 7.50 | 1.80 | 19.3 | 800 |
| 500 | 42.1 | 11.7 | 7.62 | 2.12 | 21.8 | 850 |
| 500 | 43.7 | 13.6 | 7.84 | 2.44 | 23.8 | 900 |

TABLE IV.

| Vol. of gas aspirated. ccs. | Vol.of $SO_2$ ccs. | VOL.of $SO_3$ ccs. | $\%SO_2$ | $\%SO_3$ | % Conversion $SO_2$ to $SO_3$ | Temp. of Furnace. $^oC.$ |
|---|---|---|---|---|---|---|
| 500 | 18.6 | Trace | 3. 59 | - | - | 150 |
| 500 | 19.2 | Trace | 3.70 | - | - | 200 |
| 500 | 23.7 | Trace | 4.42 | - | - | 250 |
| 500 | 25.1 | 5.8 | 4.66 | 1.09 | 18.8 | 300 |
| 500 | 26.8 | 6.7 | 5.04 | 1.26 | 20.0 | 350 |
| 500 | 26.9 | 7.9 | 5.05 | 1.48 | 22.8 | 400 |
| 500 | 27.2 | 8.2 | 5.07 | 1.53 | 23.2 | 450 |
| 500 | 27.75 | 8.3 | 5.17 | 1.55 | 23.0 | 500 |
| 500 | 34.2 | 8.7 | 6.30 | 1.60 | 20.2 | 550 |
| 500 | 34.7 | 9.1 | 6.40 | 1.68 | 20.8 | 600 |
| 500 | 36.3 | 9.1 | 6.66 | 1.67 | 20.0 | 650 |
| 500 | 37.8 | 10.4 | 6.90 | 1.90 | 19.6 | 700 |
| 500 | 40.7 | 12.3 | 7.36 | 2.22 | 23.2 | 750 |
| 500 | 46.1 | 15.7 | 8.23 | 2.80 | 25.4 | 800 |
| 500 | 46.6 | 17.8 | 8.28 | 3.16 | 27.7 | 850 |
| 500 | 46.4 | 19.1 | 8.20 | 3.2 | 29.2 | 900 |

TABLE V.

| Vol.of gas aspirated. | Vol. of $SO_2$ ccs. | Vol.of $SO_3$ ccs. | % $SO_2$ | % $SO_3$ | % Conversion $SO_2$ to $SO_3$ | Temp. of Furnace. °C. |
|---|---|---|---|---|---|---|
| 500 | 21.3 | Trace | 4.10 | - | - | 150 |
| 500 | 22.6 | Trace | 4.30 | - | - | 200 |
| 500 | 27.56 | 6.4 | 5.10 | 1.20 | 18.9 | 250 |
| 500 | 28.50 | 7.1 | 5.32 | 1.33 | 20.0 | 300 |
| 500 | 29.10 | 7.6 | 5.43 | 1.42 | 20.7 | 350 |
| 500 | 29.80 | 8.1 | 5.54 | 1.50 | 21.1 | 400 |
| 500 | 32.0 | 8.2 | 5.91 | 1.51 | 20.4 | 450 |
| 500 | 38.2 | 8.3 | 7.00 | 1.52 | 18.3 | 500 |
| 500 | 41.0 | 8.3 | 7.47 | 1.515 | 16.9 | 550 |
| 500 | 43.0 | 8.9 | 7.80 | 1.61 | 17.2 | 600 |
| 500 | 47.2 | 11.7 | 8.45 | 2.10 | 19.9 | 650 |
| 500 | 48.9 | 13.1 | 8.70 | 2.33 | 21.2 | 700 |
| 500 | 49.4 | 15.2 | 8.75 | 2.70 | 23.5 | 750 |
| 500 | 49.0 | 17.2 | 8.67 | 3.02 | 26.0 | 800 |
| 500 | 47.8 | 17.4 | 8.47 | 3.08 | 26.7 | 850 |
| 500 | 44.2 | 17.4 | 7.87 | 3.09 | 28.7 | 900 |

TABLE VI.

| Vol.of gas aspirated. | Vol. of $SO_2$ ccs. | vol.of $SO_3$ ccs. | % $SO_2$ | % $SO_3$ | % Conversion $SO_2$ to $SO_3$ | Temp.of furnace. $^oC$. |
|---|---|---|---|---|---|---|
| 750 | 6.98 | Trace | 0.92 | - | - | 300 |
| 750 | 8.25 | 5.4 | 1.08 | 0.71 | 39.6 | 350 |
| 720 | 8.93 | 6.2 | 1.21 | 0.84 | 41.0 | 400 |
| 690 | 11.92 | 8.28 | 1.68 | 1.16 | 41.0 | 450 |
| 525 | 11.70 | 7.09 | 2.16 | 1.30 | 37.8 | 500 |
| 486 | 14.10 | 7.98 | 2.78 | 1.57 | 36.2 | 550 |
| 473 | 18.70 | 7.66 | 3.77 | 1.54 | 29.2 | 600 |
| 492 | 21.80 | 9.00 | 4.17 | 1.72 | 29.2 | 650 |
| 388 | 28.90 | 7.15 | 6.82 | 1.69 | 19.8 | 700 |
| 382 | 29.10 | 8.30 | 6.95 | 1.98 | 22.2 | 750 |
| 314 | 23.90 | 9.00 | 6.89 | 2.60 | 27.4 | 800 |
| 300 | 20.4 | 9.45 | 6.20 | 2.87 | 31.6 | 850 |
| 290 | 19.2 | 9.92 | 6.02 | 3.11 | 34.1 | 900 |

TABLE VII.

| Vol.of gas aspirated. ccs. | Vol.of $SO_2$ ccs. | Vol.of $SO_3$ ccs. | % $SO_2$ | % $SO_3$ | % Conversion $SO_2$ to $SO_3$ | Temp.of furnace. $^oC.$ |
|---|---|---|---|---|---|---|
| 720 | 16.9 | Trace | 2.3 | - | - | 300 |
| 700 | 26.7 | Trace | 3.68 | - | - | 350 |
| 675 | 36.8 | 10.8 | 5.10 | 1.49 | 22.7 | 400 |
| 660 | 36.3 | 11.2 | 5.13 | 1.58 | 23.6 | 450 |
| 610 | 34.1 | 11.0 | 5.21 | 1.68 | 24.4 | 500 |
| 578 | 38.7 | 10.4 | 6.16 | 1.66 | 21.2 | 550 |
| 523 | 35.6 | 9.95 | 6.27 | 1.75 | 21.8 | 600 |
| 494 | 38.6 | 9.4 | 7.12 | 1.74 | 19.6 | 650 |
| 481 | 38.9 | 9.38 | 7.35 | 1.77 | 19.4 | 700 |
| 436 | 36.6 | 9.15 | 7.6 | 1.90 | 20.0 | 750 |
| 387 | 34.5 | 8.9 | 8.68 | 2.06 | 20.5 | 800 |
| 294 | 26.2 | 7.95 | 7.98 | 2.42 | 23.3 | 850 |
| 268 | 23.3 | 8.36 | 7.79 | 2.79 | 26.4 | 900 |

TABLE VIII.

| Vol.of gas aspirated. ccs. | Vol.of $SO_2$ ccs. | Vol.of $SO_3$ ccs. | % $SO_2$ | % $SO_3$ | % Conversion $SO_2$ to $SO_3$ | Temp. of Furnace. °C. |
|---|---|---|---|---|---|---|
| 480 | 14.9 | Trace | 3.02 | - | - | 300 |
| 472 | 21.35 | Trace | 4.35 | - | - | 350 |
| 470 | 27.7 | Trace | 5.58 | - | - | 400 |
| 420 | 25.6 | 3.78 | 5.70 | 0.84 | 12.9 | 450 |
| 390 | 24.4 | 4.13 | 5.83 | 0.99 | 14.5 | 500 |
| 375 | 28.3 | 4.10 | 6.95 | 1.00 | 12.7 | 550 |
| 312 | 23.1 | 4.47 | 6.81 | 1.32 | 16.4 | 600 |
| 295 | 23.3 | 4.28 | 7.23 | 1.32 | 15.6 | 650 |
| 234 | 19.4 | 3.40 | 7.55 | 1.32 | 15.0 | 700 |
| 196 | 17.1 | 3.50 | 7.87 | 1.62 | 17.0 | 750 |
| 150 | 13.6 | 2.88 | 8.17 | 1.73 | 17.5 | 800 |
| 112 | 10.1 | 2.33 | 8.10 | 1.87 | 18.7 | 850 |
| 86 | 7.74 | 2.20 | 8.06 | 2.40 | 22.0 | 900 |

SKETCH OF APPARUTUS

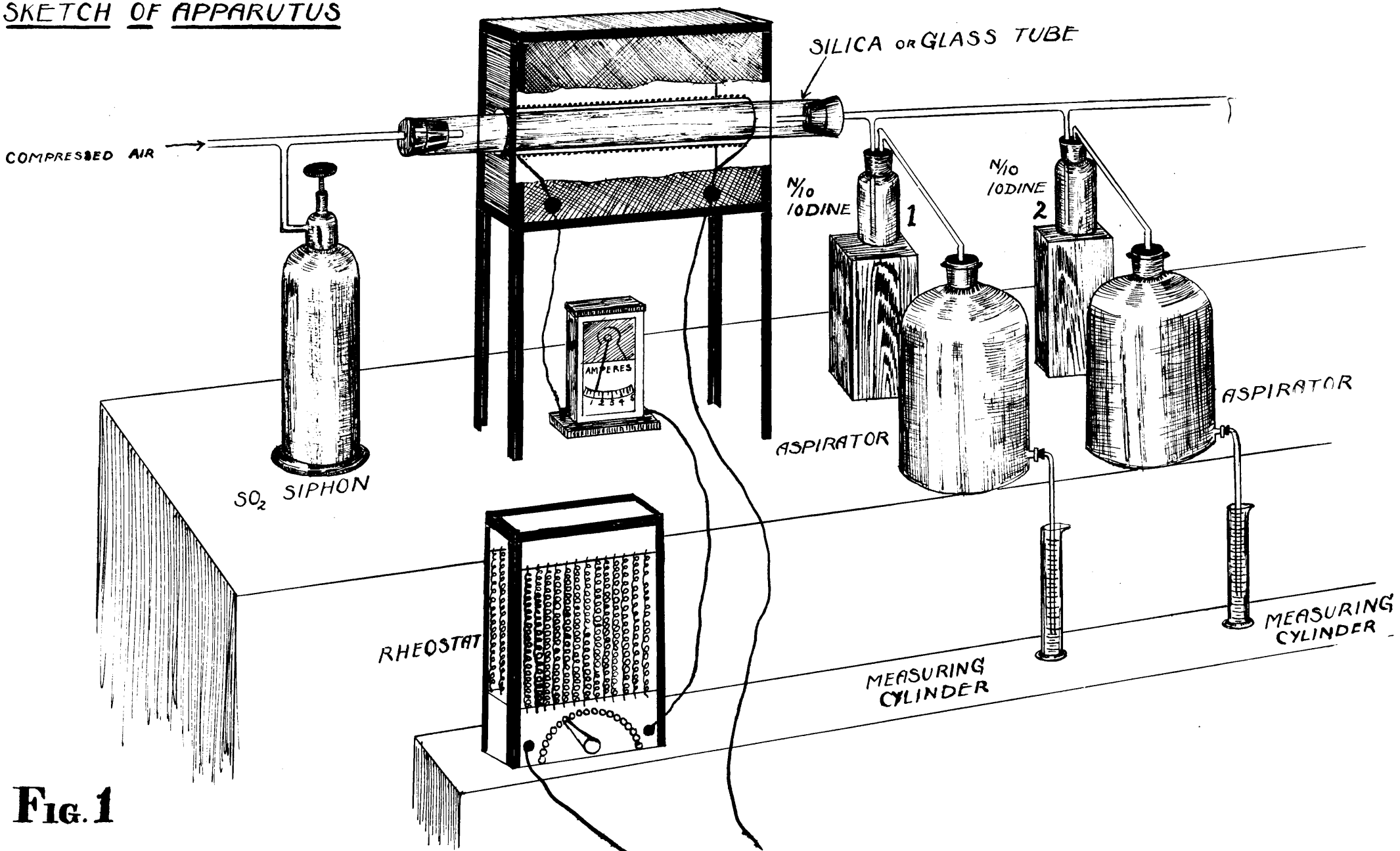



**FIG. 1**

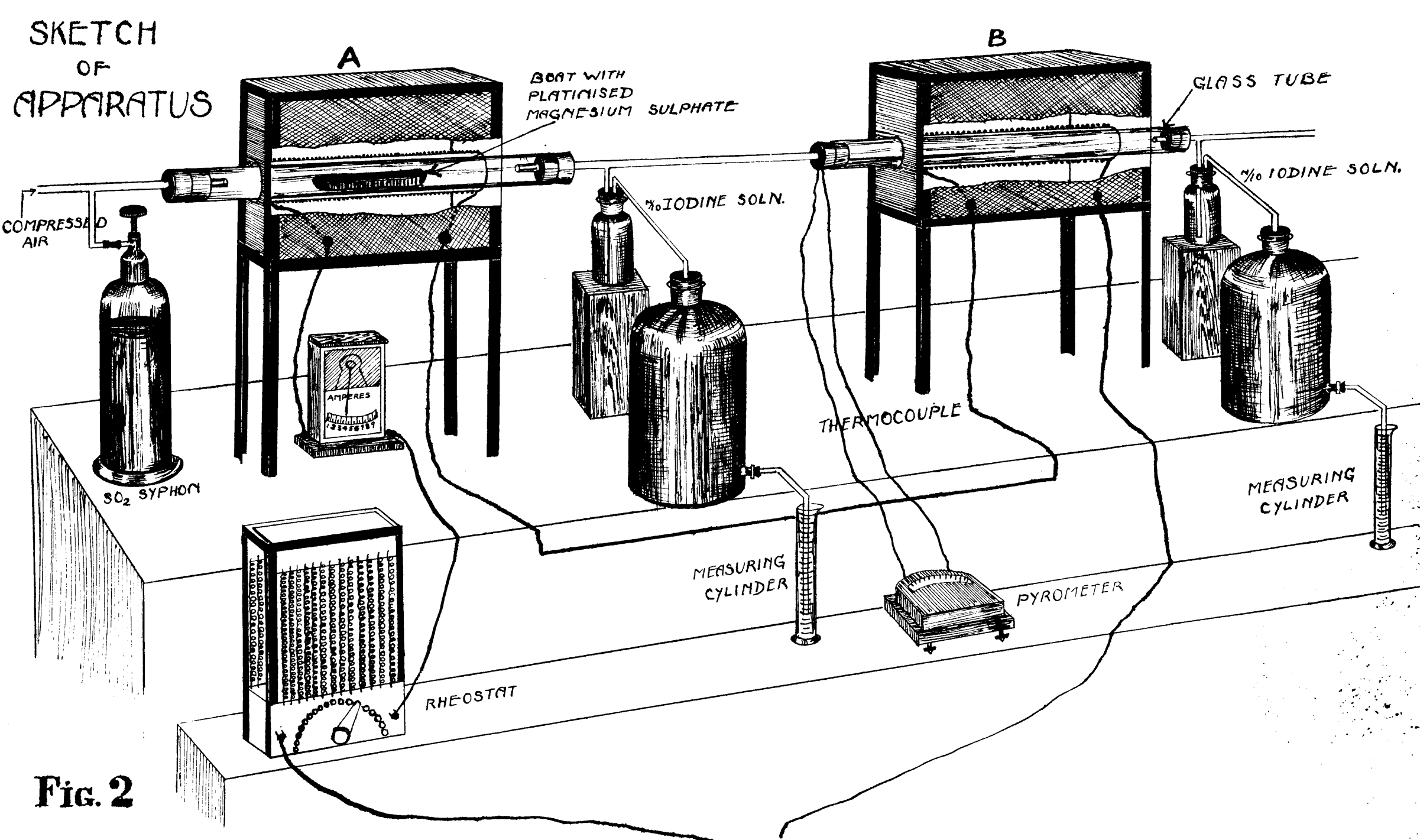

SKETCH
OF
APPARATUS
A
B
BOAT WITH
PLATINISED
MAGNESIUM SULPHATE
GLASS TUBE
COMPRESSED
AIR
% IODINE SOLN.
% IODINE SOLN.
AMPERES
THERMOCOUPLE
$SO_2$ SYPHON
MEASURING
CYLINDER
MEASURING
CYLINDER
PYROMETER
RHEOSTAT

**Fig. 2**

# SKETCH OF APPARATUS

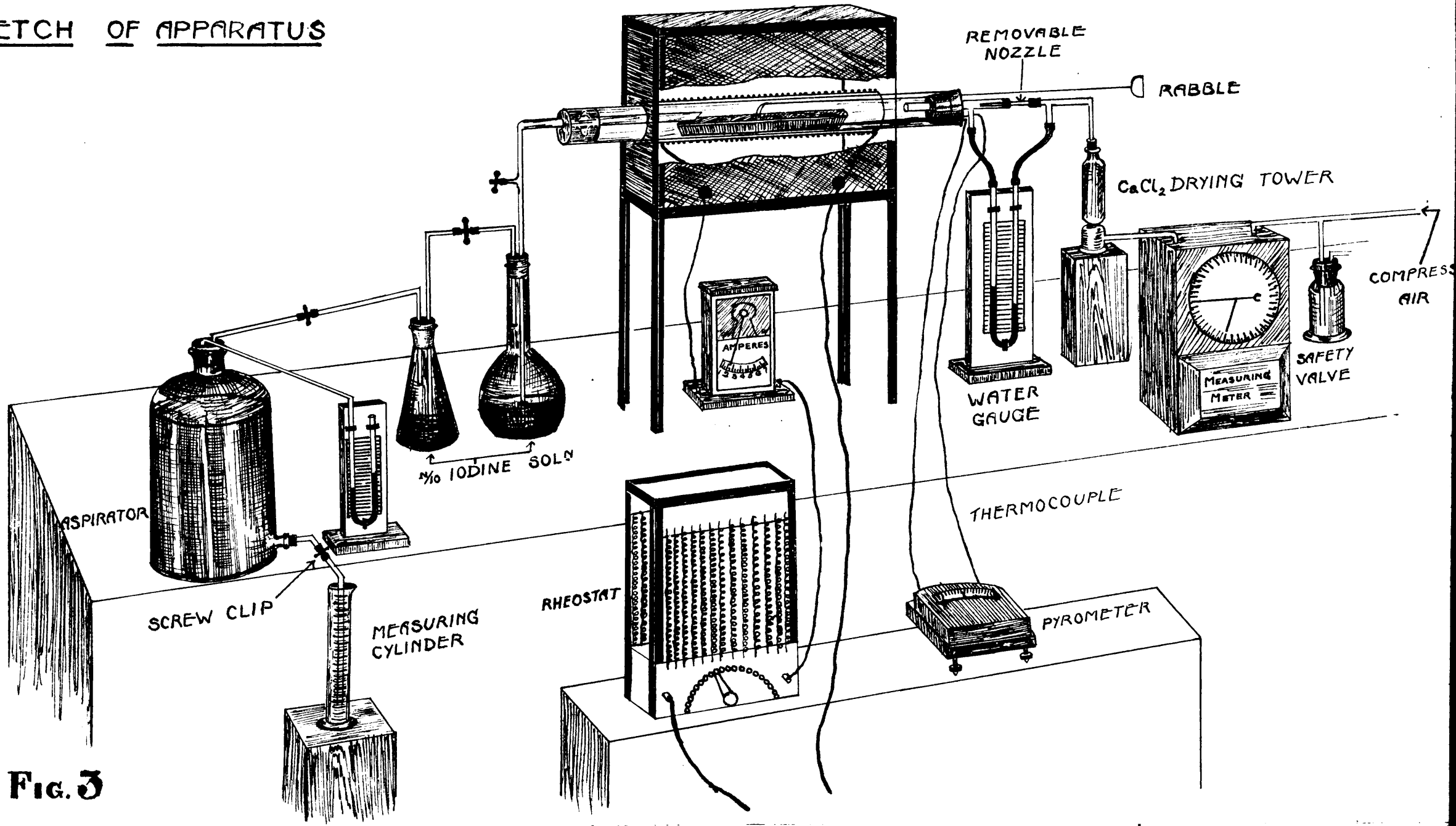
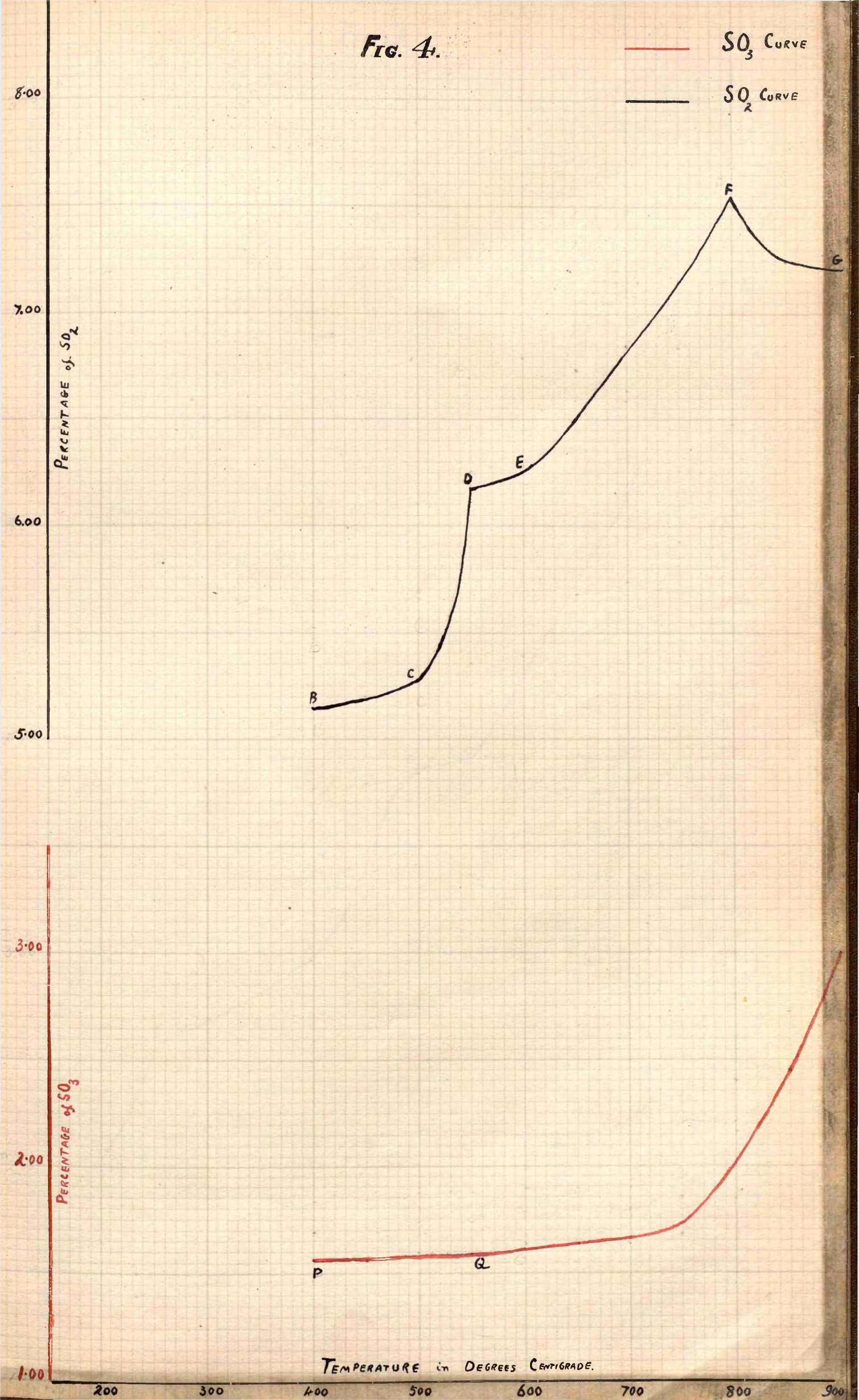


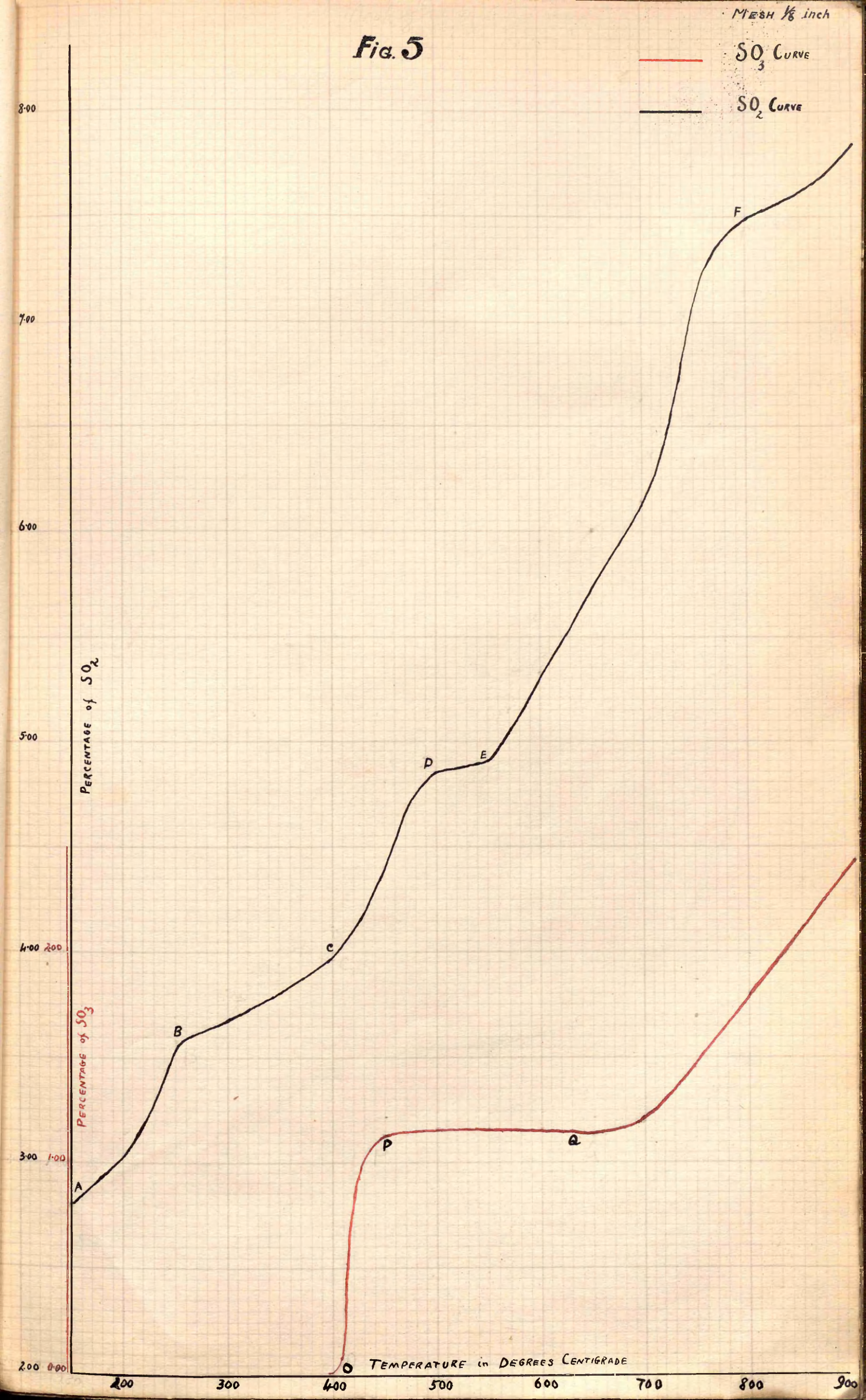

FIG. 3

# Fig. 4.


SO3 Curve
SO2 Curve
8·00
7·00
6·00
5·00
Percentage of SO2
B
C
D
E
F
G
3·00
2·00
1·00
Percentage of SO3
P
Q
Temperature in Degrees Centigrade.
200
300
400
500
600
700
800
900

MESH 1/8 inch

# Fig. 5

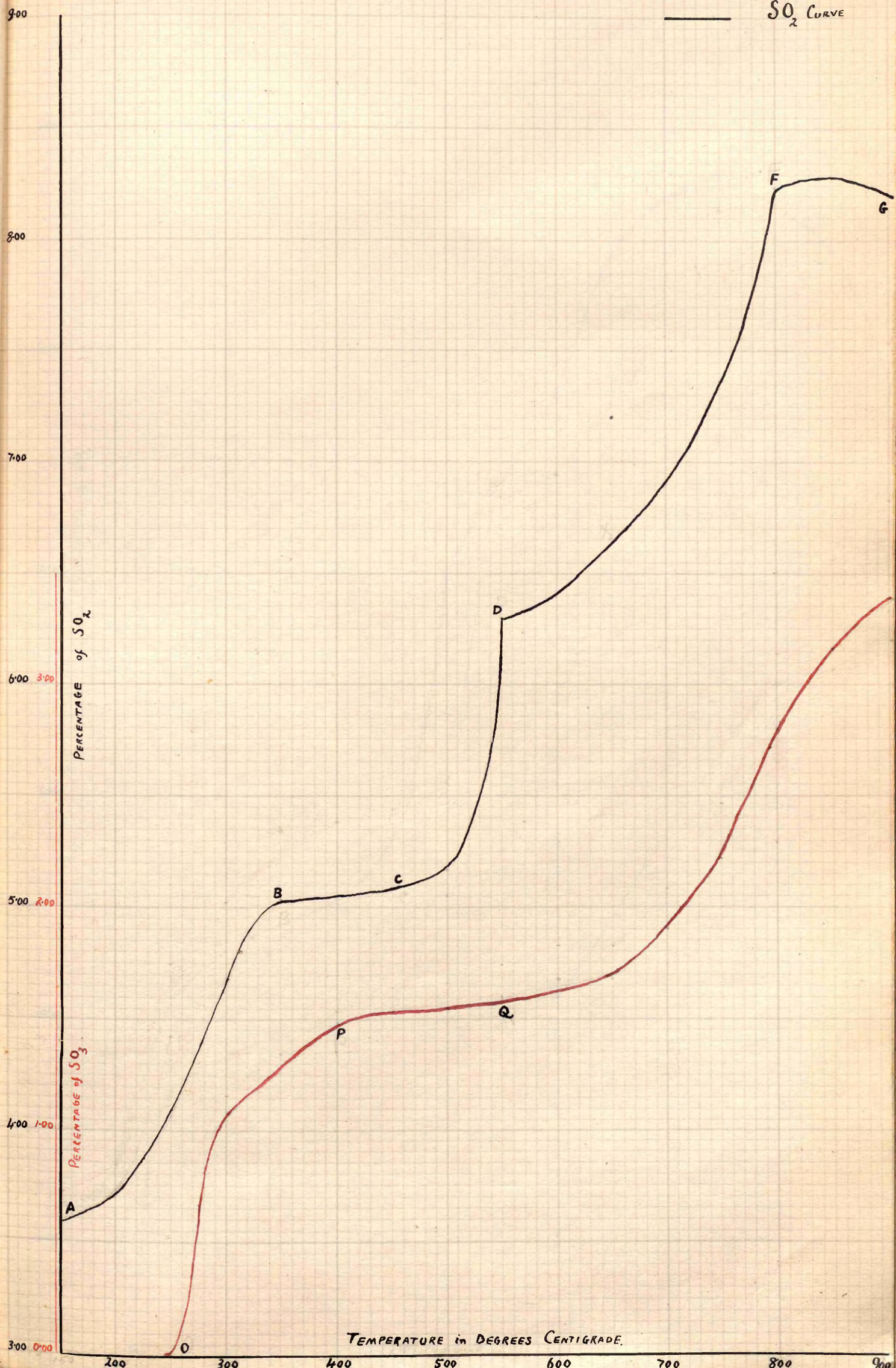


MESH 10

# Fig. 6

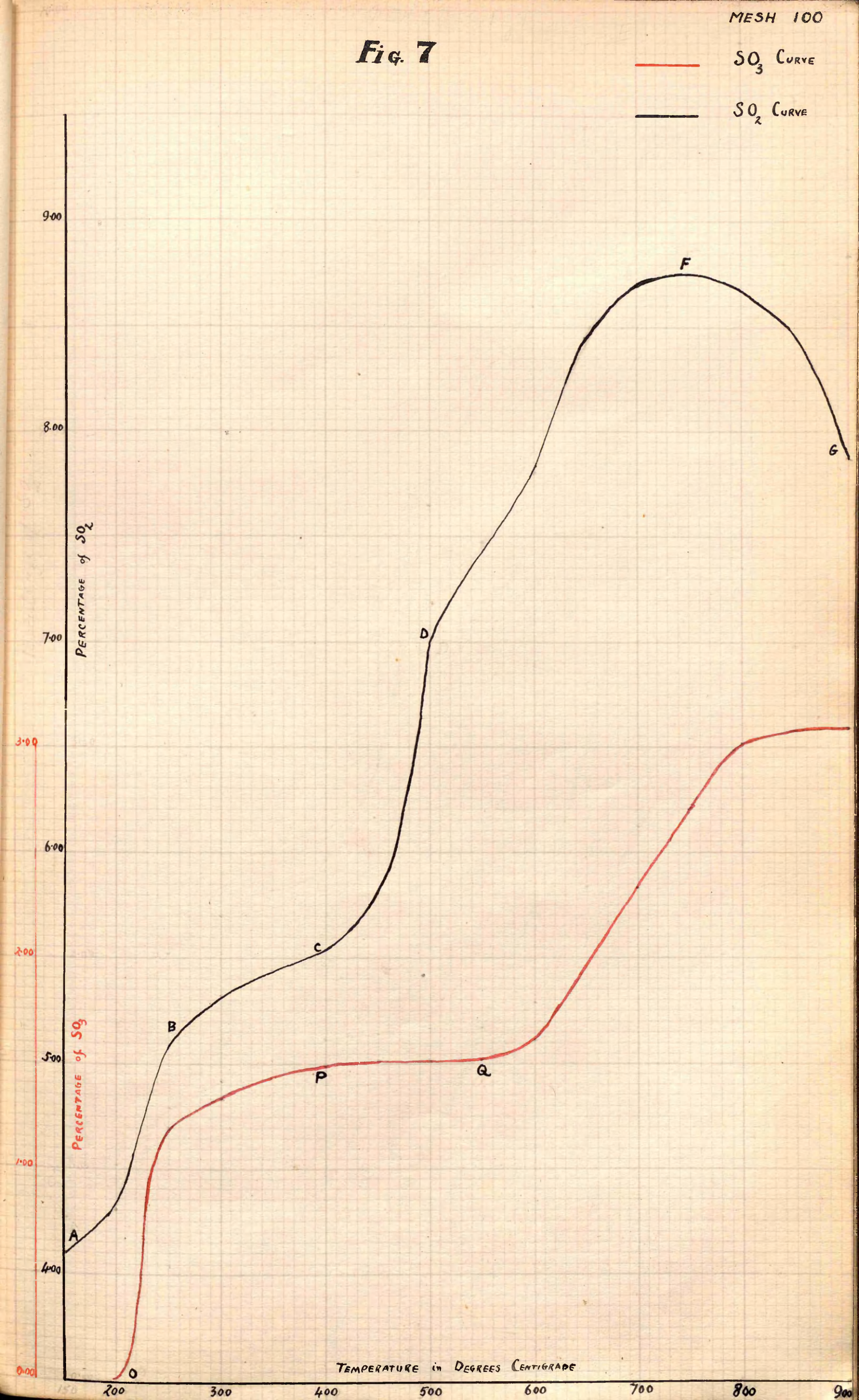
$SO_3$ Curve

$SO_2$ Curve

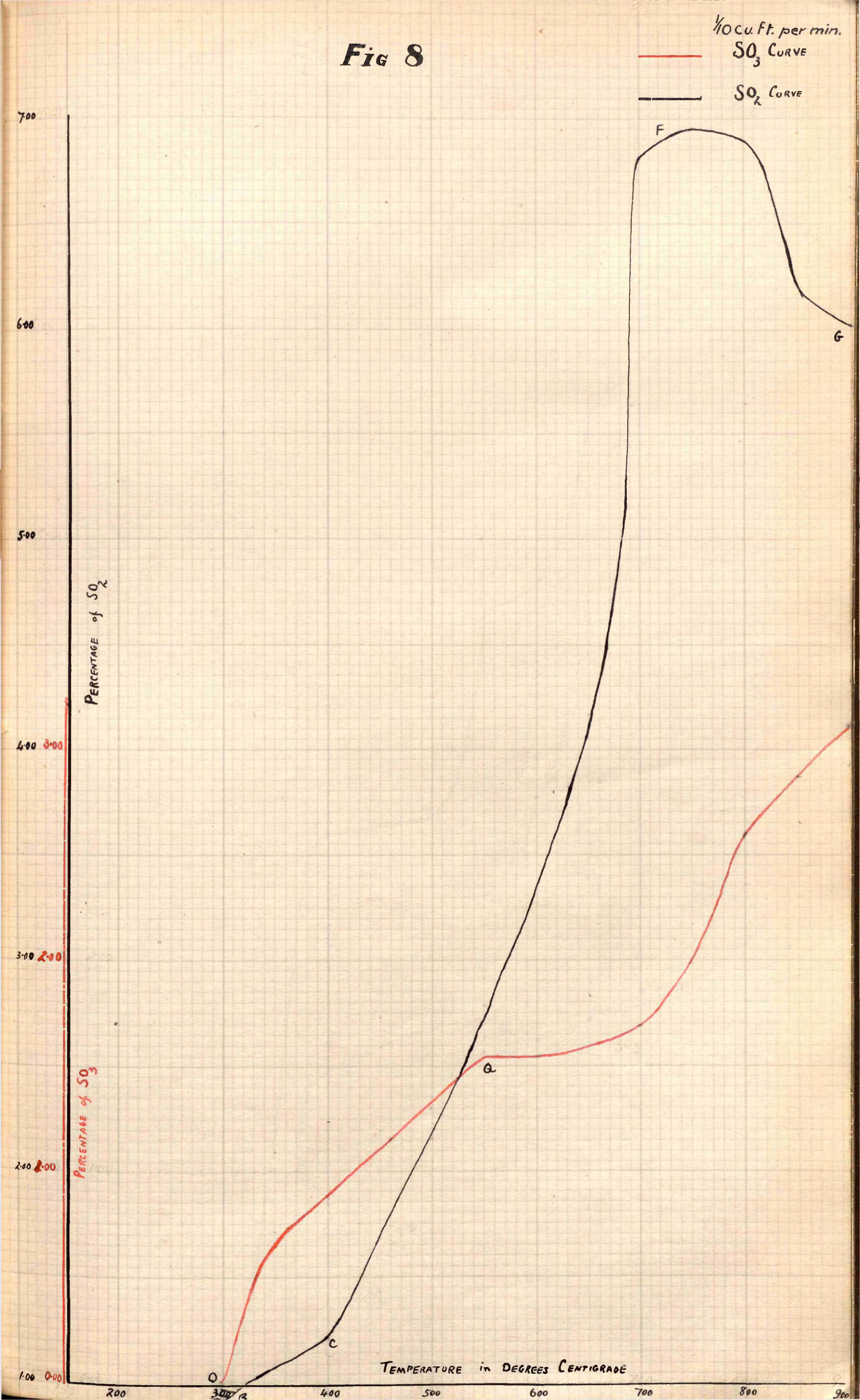


MESH 100

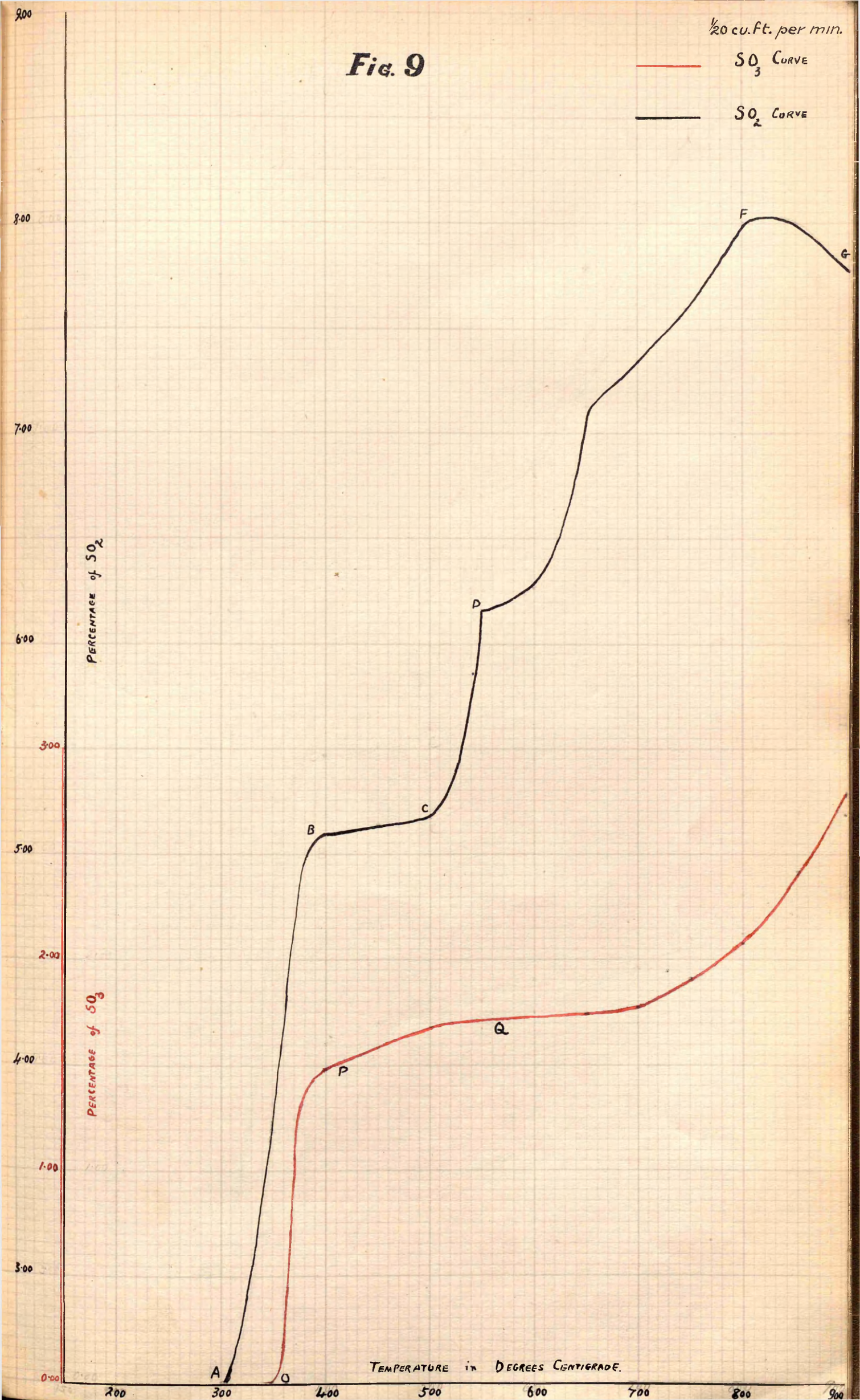
# Fig. 7



# Fig 8


1/10 cu. ft. per min.
SO3 Curve
SO2 Curve
7·00
6·00
5·00
4·00
3·00
2·00
1·00
0·00
3·00
2·00
1·00
0·00
Percentage of SO2
Percentage of SO3
F
G
Q
C
O
R
200
300
400
500
600
700
800
900
Temperature in Degrees Centigrade

# Fig. 9

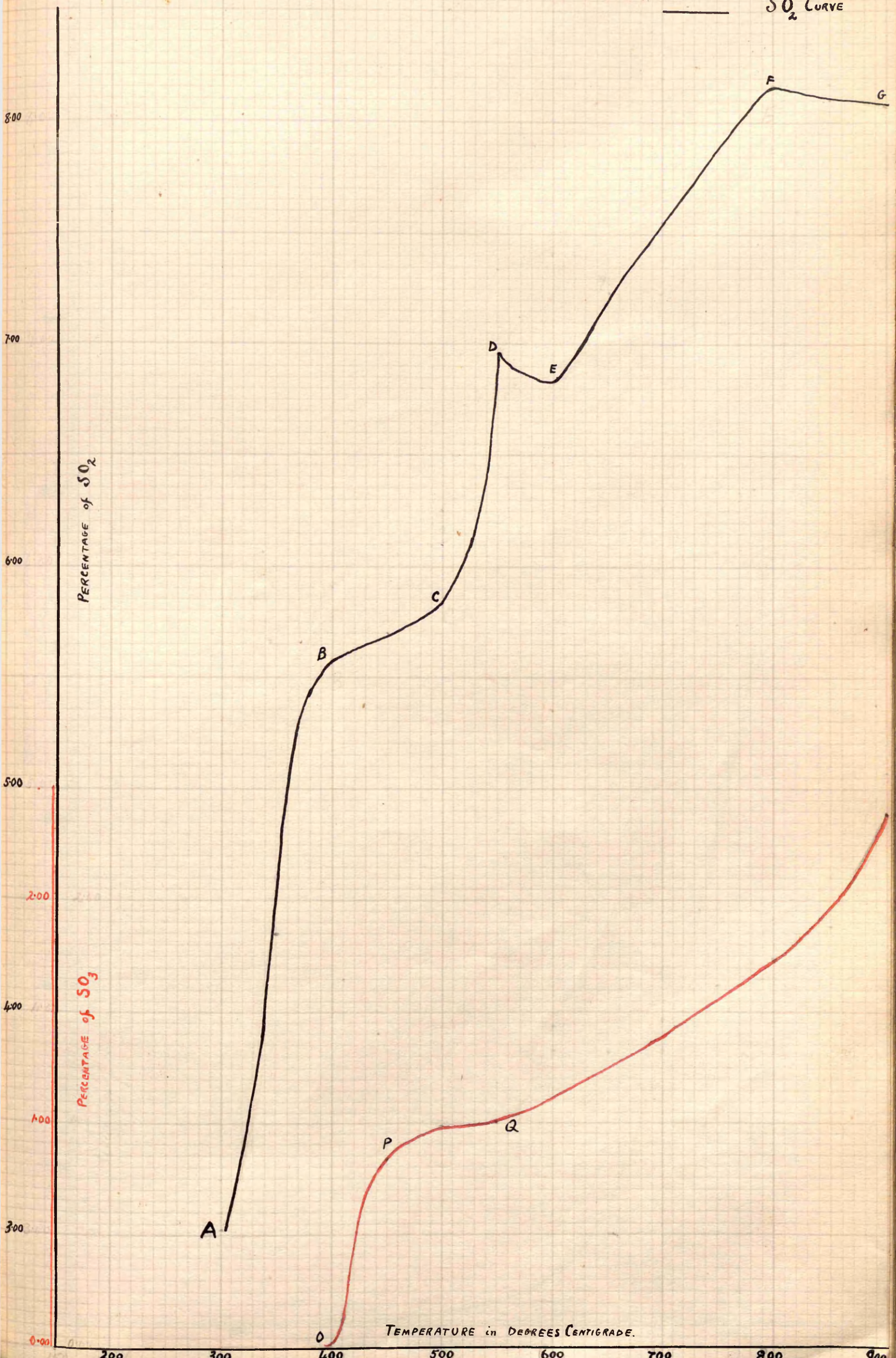

1/20 cu. ft. per min.
$SO_3$ Curve
$SO_2$ Curve
9·00
8·00
7·00
6·00
5·00
4·00
3·00
2·00
1·00
0·00
Percentage of $SO_2$
Percentage of $SO_3$
A
B
C
D
F
G
O
P
Q
200
300
400
500
600
700
800
900
Temperature in Degrees Centigrade.

# Fig. 10

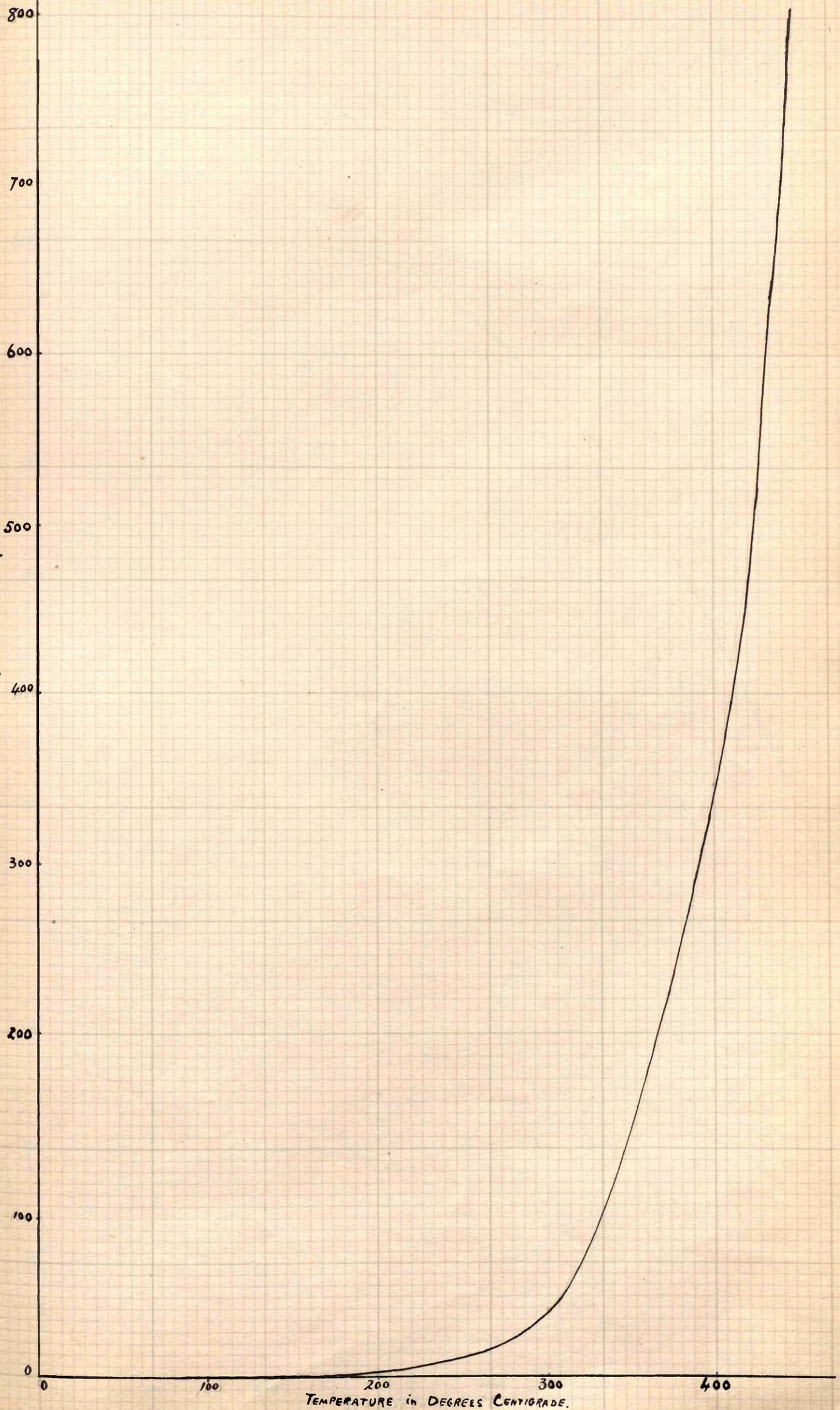
1/30 cu. ft. per min.

$SO_3$ Curve

$SO_2$ Curve



# Fig 11


800
700
600
500
400
300
200
100
0
Vapour Pressure of Sulphur in m/m.
0
100
200
300
400
Temperature in Degrees Centigrade.

# Fig 12

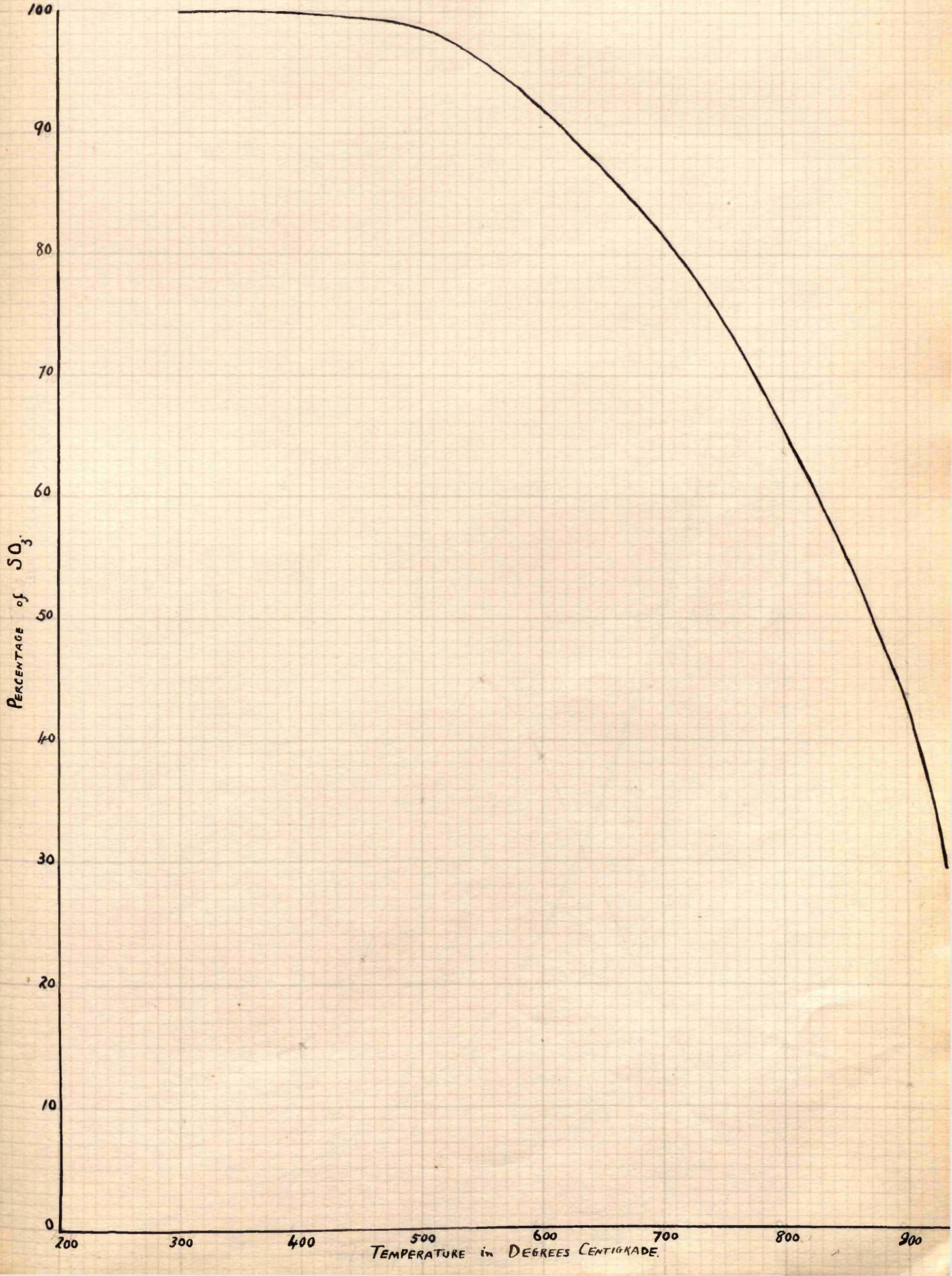
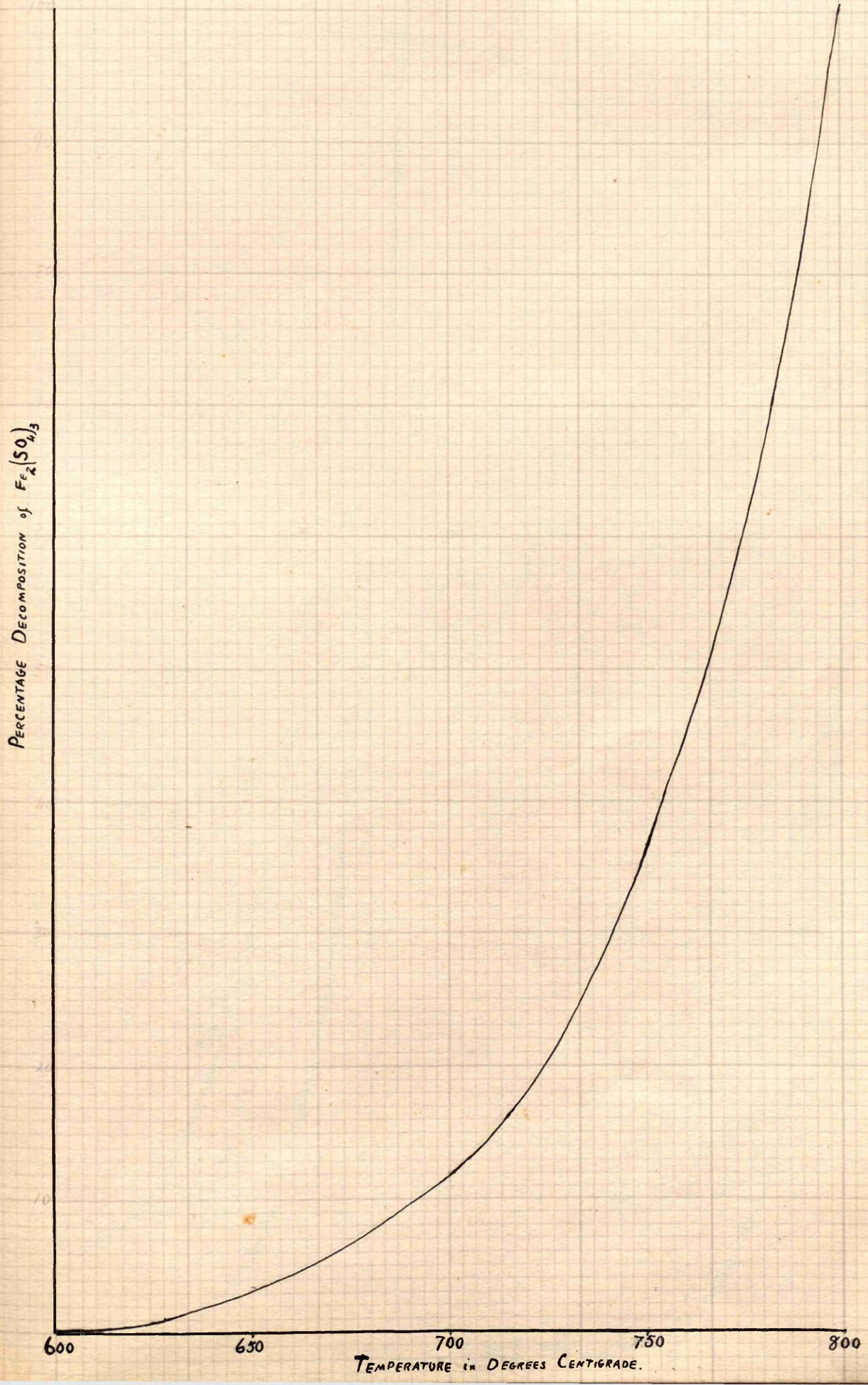
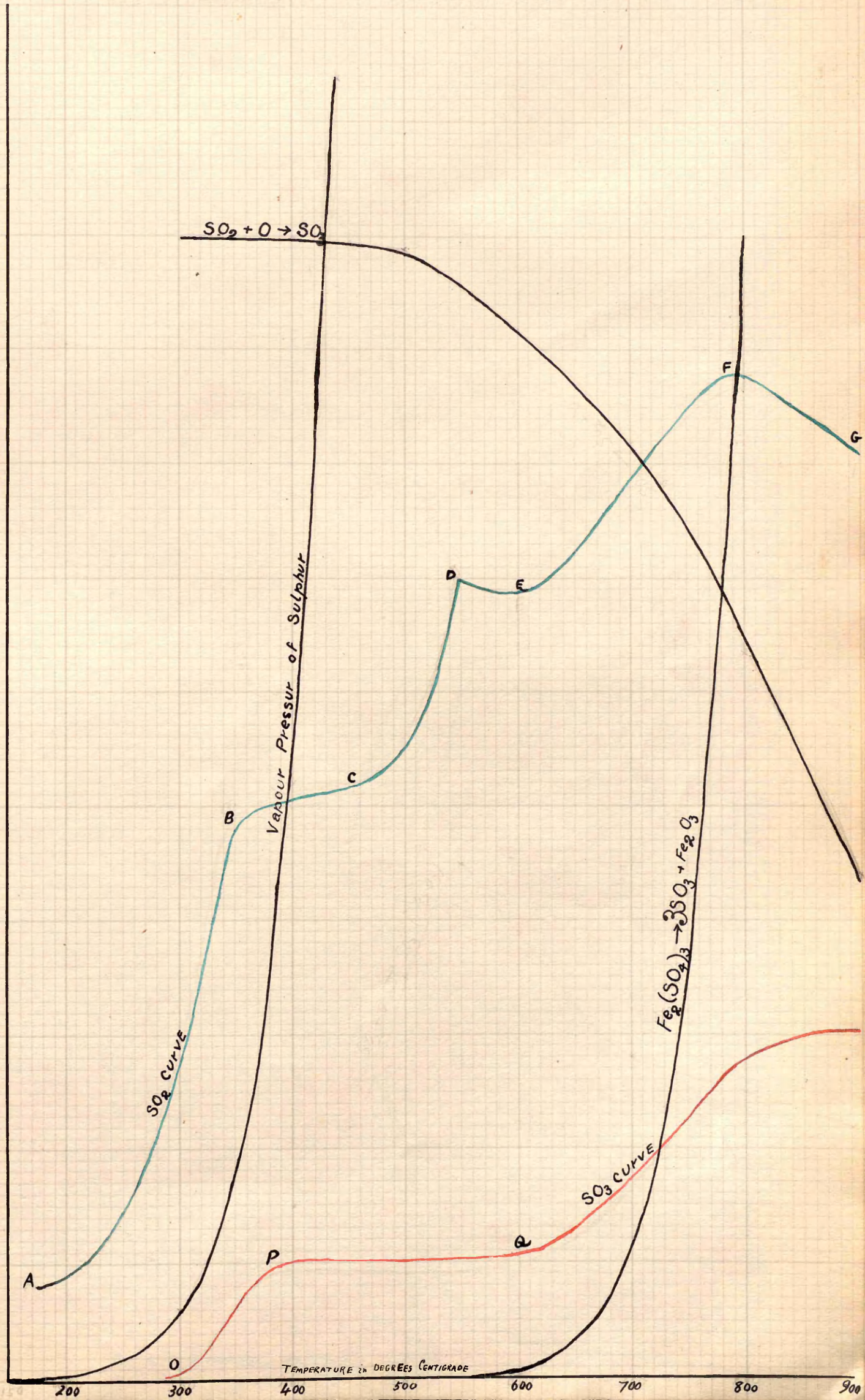

100
90
80
70
60
50
40
30
20
10
0
Percentage of $SO_3$
200
300
400
500
600
700
800
900
Temperature in Degrees Centigrade.

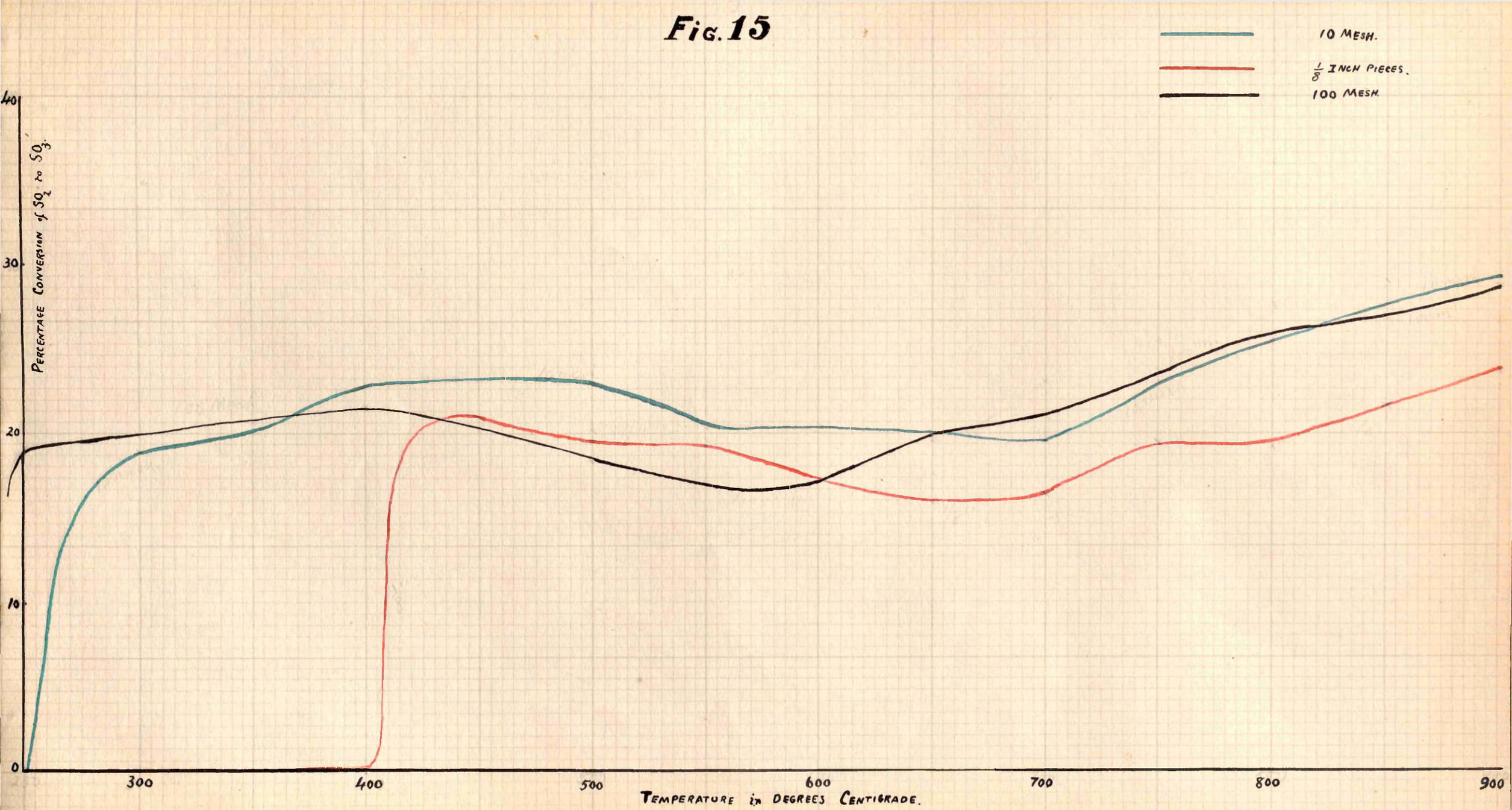
Fig 13


Percentage Decomposition of $Fe_2(SO_4)_3$
600
650
700
750
800
Temperature in Degrees Centigrade.

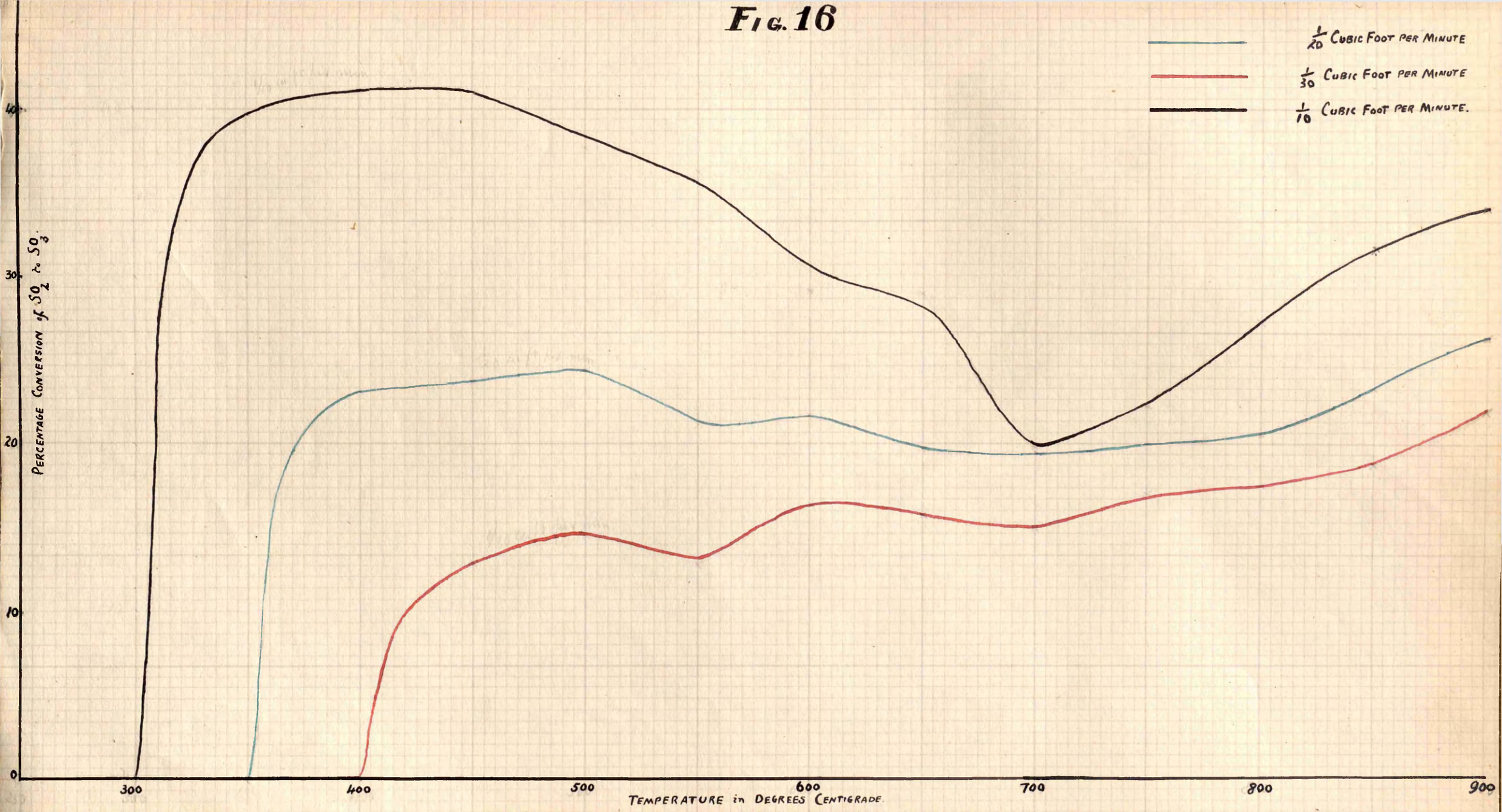
# Fig. 14


$SO_2 + O \rightarrow SO_3$
Vapour Pressur of Sulphur
$Fe_2(SO_4)_3 \rightarrow 3SO_3 + Fe_2O_3$
$SO_2$ curve
$SO_3$ curve
A
B
C
D
E
F
G
O
P
Q
Temperature in degrees Centigrade
200
300
400
500
600
700
800
900

# Fig. 15


10 Mesh.
1/8 Inch Pieces.
100 Mesh.
Percentage Conversion of $SO_2$ to $SO_3$.
40
30
20
10
0
300
400
500
600
700
800
900
Temperature in Degrees Centigrade.

# Fig. 16


1/20 Cubic Foot per Minute
1/30 Cubic Foot per Minute
1/10 Cubic Foot per Minute.
Percentage Conversion of $SO_2$ to $SO_3$.
40
30
20
10
0
300
400
500
600
700
800
900
Temperature in Degrees Centigrade.

# PART 11.

## A Study of the Effect of High Temperature upon the Constitution of Steel.

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The wide variation in the results obtained by different workers in the fields of mechanical and physical testing of heat-treated steels is well known. In many cases these differences can be accounted for by the variations in the treatment. In impact test figures, especially of the low carbon steels, the figures obtained show this in a very marked manner. Knowing how difficult it is to heat-treat the low carbon steels and so bring about much change in their constitution, and if heating above the $A_3$ line brings about homogeneity of structure, it is most difficult to account for these wide variations in the figures obtained unless on the probable grounds of grain size.

With a view to throwing some light upon the very great inconsistencies of the figures obtained from the impact tests a series of experiments was designed. In drawing up the scheme of work, particular care was given to the heat treatment so that as wide a variety of structures as possible might be obtained. By such a scheme it was hoped to be able to correlate impact value with micro-structure.

Three steels of varying carbon content and low in manganese were selected. The steels were of crucible manufacture and in the form of rolled bars, one inch in diameter. The analyses of the steels are given in Table I.

Table I.

| Sample No. | Carbon. | Manganese. | Sulphur. | Phosphorus. | Silicon. |
|---|---|---|---|---|---|
| A. | 0.22 | 0.08 | 0.03 | 0.03 | 0.15 |
| B. | 0.48 | 0.18 | 0.03 | 0.03 | 0.11 |
| C. | 0.71 | 0.15 | 0.03 | 0.03 | 0.10 |

The bars were cut into five-inch lengths and heat treated before machining. The test piece was of the usual Izod form, 10 m.m. square, with a 45 degree notch, 2 m.m. deep and a radius/

radius at the bottom of the V of 0.25 m.m.

The treatments at 1100°C. were carried out in a large gas-fired Richmond furnace and the specimens were packed in bone ash in an iron box to minimise oxidation. The temperature of the furnace was measured by means of a Cambridge optical pyrometer. All other treatments were carried out in silica tube electric furnaces of the resistance type, and the temperature was measured by means of a Platinum, Platinum-Iridium thermocouple and indicator, the couple having been standardised before use. The heat treatment given to the individual bars is shown in Table II.

Table II.

| No. of sample. | |
|---|---|
| A1, B1, C1 | All soaked at 1100°C. for 3 hours and then allowed to cool very slowly in the furnace. |
| A2 | Treated as above; then re-heated to 780°C. for 20 minutes and cooled in the furnace. |
| B2 | Treated as above, then re-heated to 730°C. for 20 minutes and cooled in the furnace. |
| C2 | Treated as above, then re-heated to 710°C. for 20 minutes and cooled in the furnace. |
| A3, B3, C3 | All soaked at 1100°C. for 3 hrs. as above specimens; then tempered at 650°C. for 12 hours. |
| A4 | Oil-hardened from 870°C. and tempered at 650°C. for half an hour. |
| B4 | Oil-hardened from 810°C. and tempered at 650°C. for half an hour. |
| C4 | Oil-hardened from 770°C. and tempered at 650°C. for half an hour. |
| A5 | Oil-hardened from 870°C. and tempered at 650°C. for 12 hours. |
| B5 | Oil-hardened from 810°C. and tempered at 650°C. for 12 hours. |
| C5 | Oil-hardened from 770°C. and tempered at 650°C. for 12 hours. |

The treatments fell into two wide groups; one in which the steels after soaking for 3 hours at 1100°C. were slowly cpoled and then, either tested in that state, or re-heated to 20°C. below the upper critical point for 20 minutes or to 650°C. for 12 hours; the second group in which the steels were oil-hardened from 50°C. above the upper critical point and tempered either at 650°C. for ½ an hour or at 650°C. for 12 hours. The

critical points of the steels were determined from cooling curves.

Table III.

| Sample No. | Treatment. | 1. | 2. | 3. | Aver. | Micro No. | Micro-structure. |
|---|---|---|---|---|---|---|---|
| A1 | Soaked at 1100°C. for 3 hrs and furnace cooled. | 6¼ | 5½ | 6½ | 6 | 1. | Ferrite grains with Pearlite at the boundaries. |
| B1 | | 3½ | 2½ | 4½ | 3½ | 2. | Large Pearlite grains and massive ferrite at the boundaries. |
| C1 | | 1 | ½ | 1 | 1 | 3. | Lammelar Pearlite in large grains, with massive ferrite at the boundaries. |
| A2 | Soaked at 1100°C. for 3 hours. | 10 | 10 | 10 | 10 | - | Very similar to No. 1. |
| B2 | Reheated to 20°c. below $Ar_3$ for 20 minutes. | 2½ | 1½ | 1½ | 2 | 4. | Coarse structure, ferrite boundaries not absorbed. |
| C2 | | 6½ | 7½ | 5½ | 6½ | - | Similar to micro.4 but more pearlite. |
| A3 | Soaked at 1100°C. for 3 hours; | 11 | 10½ | 9 | 10 | - | Similar to micro.1. |
| B3 | Tempered 650°C. for 12 hours. | 2½ | 1½ | 1½ | 2 | - | Similar to micro.2. |
| C3 | | 5½ | 5 | 4½ | 5 | - | Similar to micro.3. |
| A4 | O.H. from 50°C. above $Ac_3$; | 89 | 90 | - | 90 | 5. | Ferrite grains with well-distributed pearlite. |
| B4 | Tempered 650°C. for 30 minutes. | 10 | 21½ | 19 | 20 | 6. | Well distributed ferrite and pearlite in small grains. |
| C4 | | 8½ | 8½ | 7½ | 8 | 7. | Finely distributed ferrite and pearlite. |
| A5 | O.H. from 50°C. above $Ac_3$; | 96 | 96 | 96 | 96 | - | Similar to micro.5. |
| B5 | Tempered 650°C. for 12 hours. | 16 | 16 | 14 | 16 | - | Similar to micro.6. |
| C5 | | 8½ | 8½ | 11½ | 9 | - | Similar to micro.7. |

The results obtained from the impact tests and from micro-examination are stated in tabular form in table III. The average impact figure is the average of the three results obtained for each specimen. In all cases the agreement between the three results was remarkably close. The impact results are also represented graphically in figure 1.

The outstanding feature of the results is the marked groups into which they fall and these groups appear to depend only upon the initial treatment. Those steels which were soaked at 1100°C. and slowly cooled continued to give low impact values even after tempering for 12 hours at 650°C., and, still more remarkable, even after heating to within 20°C. of the upper critical point. On the other hand the steels which were taken just above the change point gave good results and tempering for a long time did not improve their value. It is worthy of note that the results obtained by Dr Hatfield for a series of carbon steels normalised from 50°C. above the upper critical point gave almost identical results to those obtained in the above table for oil-hardening. (See Journ.I. & S.Inst. W.of Scot.Vol.XXVIII Pt.5). It is further to be noted that as the carbon content increases the difference between the two groups becomes less. This is not surprising as the quantity of carbide of iron being high only very small impact figures can be expected.

The wide difference between the results of the low carbon steel in the two groups could not be attributed to difference in grain size. This can be seen by comparing photo-micrographs 1 and 5. On careful examination it was observed that in the low carbon steels which had been heated to 1100°C., the pearlite was somewhat divorced and that many of the grains were surrounded, or partly surrounded, by a film of carbide of iron. In photo-micrograph No.8 is shown one of these carbide films.

The effect of high temperature is still further exemplified in the case of steel castings. These, owing to the slow rate of cooling, develop the effect of the high temperature in a marked degree and in an impact test give about 3 ft. lbs as an average value. Heating such a casting of 0.27°C. content to 900°C. and cooling in the furnace gave a value of 6.5 ft. lbs whilst heating a second time to 900°C. and cooling in air gave 27 ft. lbs. The effect of the double annealing has been to break down the carbide films, two treatments accomplishing this more effectively than one.

This/

This is clearly shown in photomicrographs Nos. 9, 10, 11.

That the separation of a film of iron carbide at the grain boundaries may be of far-reaching industrial importance was revealed by the examination of some boiler plate failures. A number of these showed distinct boundaries of iron carbide round the grains. Figure 12 shows one typical case, its carbon content being 0.18% carbon, and the sulphur phosphorus and manganese normal.

The next problem was to investigate the formation of these boundary films. Do they form at high temperatures or do they separate when passing through the $Ar_1$ point? From the impact results, in relation to their treatment, it would appear most probable, that they are formed at elevated temperatures.

Three specimens were cut off the same bars as those used for the impact experiments. The specimens were approximately $\frac{1}{8}$" in thickness. These were put into a double tube electric resistance furnace, the inner tube of which was of Royal Berlin Porcelain. One end of the furnace was connected to a Töpler pump. To the other end was attached a closed glass vessel containing iodine, there being a glass stop-cock between the vessel and the furnace. The specimens were placed in the centre of the furnace and the tube evacuated. The furnace was heated to 1100°C, the temperature being measured by a thermo-couple, and maintained at this temperature for six hours, a high vacuum being maintained throughout the experiment. The vessel containing the iodine was warmed, all air was displaced by iodine vapour before coupling to the furnace — then the stop-cock was opened and the iodine allowed to pass into the furnace. The specimens were immediately quenched in water. In the first attempts the iodine etching/

etching was overdone but latterly good results were attained. Figs.13 and 14 show the results obtained for the steels containing 0.22%C and 0.48%C respectively. The high temperature configuration is clearly marked.

Without in any way interfering with the etching, these specimens were replaced in the cold furnace. The furnace was again evacuated and then heated to 650°C. This temperature was maintained for four hours and the specimens cooled in the furnace. Photomicrographs Nos. 15 and 16 show the results obtained. In Fig.15 the recrystallisation is clearly seen. It is also to be noted that in the black portions designating the high temperature boundaries the carbide is distinctly segregated. It is balled up to a certain extent but this no doubt has arisen from the rather prolonged soaking. The reason for the prolonged tempering was that in some other experiments on the same steels it was found difficult to get the carbide to separate in short periods of tempering. In Fig.16 there is also evidence of carbide at the original boundaries but it is very much less evident and is much more distributed throughout the mass. In photomicrograph No.17 is shown the result obtained by heating a piece of the 0.22% C. steel in a crucible, packed in lime and having the lid luted on. The specimen was heated to 1050°C for 3 hours, and then slowly cooled in air. Before being polished the specimen was cut into two portions and the cut face of one piece was used for micro examination. Again the carbide boundaries are very clearly marked.

Repeating the above experiment with a piece of the 0.48% C steel produced a most remarkable structure as shown in photomicrograph No.18. The micro has the appearance of a 0.71% C. steel and it was thought that a mistake in the specimen treated had been made. An analysis of some drillings/

drillings taken from the specimen showed it to be 0.48%C carbon. Another specimen of the same steel was heated in a similar manner but on this occasion it was soaked at 1050°C for 15 minutes. The micrographical appearance of this specimen was very different from the previous specimen. In this case the specimen appeared patchy, some parts appearing as in Figure 18, but in others a large amount of ferrite and coarse pearlite appeared. Fig.19 shows a typical field of the specimen. These experiments appear to be substantial proof of the statement made by Andrew and his collaborators (Journ. of Iron and Steel Inst. 1920. No.1.) to explain the dilatation curves of the carbon steels. In the case in point, by subjecting the 0.48% C steel to a prolonged soaking at 1050°C all the iron carbide has become dissociated, whereas on heating for a shorter period, the dissociation has not been complete. Upon cooling in the first case the carbide particles which separate do not have time to coalesce into large colonies of massive cementite whereas in the second case where dissociation and diffusion have not been completed, more massive cementite occurs. The dissociation can be written in the form of an equation

$(Fe_3C)_x = x\ Fe_3C$. where x is most probably equal to 4, this figure being supported by theoretical calculation and by X-ray analysis.

Further evidence in favour of the view of the dissociation was obtained from thermal analysis. A specimen of the 0.22%C steel was heated to 880°C and the cooling curve was determined using a platinum, platinum-iridium thermocouple and a Tinsley Potentiometer. The $Ar_3$ and $Ar_1$ points occurred at 830°C and 700°C respectively. The same specimen was heated to 1000°C and maintained at this temperature for two hours. The cooling curve was determined/

determined as before but this time $Ar_1$ point occurred at 825°C whereas the $Ar_3$ point occurred at 700°C as formerly. Both curves were repeated a second time. The curves are shown in Fig.2. In this case the prolonged at 1000°C has caused complete dissociation and diffusion of the carbide and this finely dispersed carbide has lowered the initial change point by 5°C.

The formation of the cementite layer at the boundary of the high temperature crystals would appear to depend upon the dissociation of the carbide molecules and then the migration of the dissociated molecules to the boundaries. Actually it would not be necessary for the molecule $Fe_3C$ to move as a whole to the boundary but merely for the carbon atom to change its position. It is the general opinion, at present, that the carbon atom is outside of the lattice of the iron atoms but as Andrew has shown (Journ. Royal Technical College, Vol.2.) it may very possibly be attached to the corner atoms, a view also shared by Foley (Trans. Amer. Inst. Min. Eng. Oct. 1925.)

Langmuir has suggested that in a crystalline element such as, for instance, a metal, the surface tends to adsorb a layer of gas one atom or one molecule thick. This surface adsorption is due to the fact that every crystalline substance possesses a particular space lattice arrangement of the atoms within the crystal. If it is imagined that a large number of crystals belonging to the cubic system are joined together, the atoms within the centre of the mass will be bound together by chemical bonds or valencies to the atoms equidistant from it in the cube. At the surface, however, the outer layer being missing, the surface atoms will possess a certain number of free valencies and will, therefore, attract to themselves any foreign surrounding atoms.

According to the Langmuir method of regarding chemical combination, Iron carbide, $Fe_3C$, should have two free valencies per molecule, or in other words, it will have two electrons too few to complete the outer ring of electrons. Moreover the face-centred lattice of iron can be considered as two interpenetrating cube lattices and in the limit we shall have one isolated cube in which each atom will have one quarter of its valencies unsaturated by other atoms. It seems most probable, therefore, that the dissociated molecules of iron carbide, or the carbon atom as such, will tend to migrate to the free surfaces of the iron crystals, forming a layer of carbide of iron.

The data for the special steels also support this view. According to Langmuir, nickel is saturated with regard to its electronic configuration, and will thus possess no free valencies. It will consequently show no tendency to migrate to the crystal boundaries, and should, therefore, not interfere with the carbide segregation, excepting in so much, as it will probably alter the conditions of diffusion. This is actually so, nickel steels behaving more or less like carbon steels.

Chromium, on the other hand, possesses four free valencies, and will therefore tend to migrate to the grain boundaries even more than the carbide of iron. It is most probable that the double carbide of chromium and iron breaks down above the critical point into iron carbide and free chromium. That this is so is evident upon taking the heating curve of a quenched chromium steel. An enormous evolution of heat is observed (at about 650°C.), this being undoubtedly due to the formation of the chromium carbide on tempering, the quenched steel containing the chromium, as such, in solution. The analytical work of Andrew and Hyman (Journ. of W.of Scot.Iron and Steel Institute Vol. XXXI) gives further support to this view. A corollary, which, of necessity, arises from this view, is that, if/

if sufficient chromium be added to the steel then, by suitable heat treatment, each grain can be surrounded by a thin layer of chromium and so give to the steel the passive qualities of chromium. Thus the rustless property of the 12 per cent. chromium steels can be explained upon this view.

Another method of viewing the formation of the carbide of iron film is from the standpoint of thermodynamics. Willard Gibbs and Kelvin showed independently from thermodynamic reasoning that if a dissolved substance had the property of lowering the surface tension of a solution, the substance would exist at a higher concentration in the surface layer than in the bulk of the solution. This can be expressed mathematically thus:-

$$U = - \frac{C}{RT} \cdot \frac{d\sigma}{dc}$$

where U = concentration of substance at the surface in gms. per sq.cm.

C = concentration of solute in solution.

T = temperature on Absolute Scale.

R = gas constant.

$\sigma$ = surface tension.

Now as C, R and T are all positive the sign, and, therefore whether positive or negative adsorption is obtained, depends upon the differential coefficient $\frac{d\sigma}{dc}$. A certain amount of experimental proof of this equation has been obtained in recent years in the realms of organic chemistry by Lewis, Donnan, and others. It is quite conceivable that the concentration of the film at the boundary might exceed saturation and precipitation take place. It has not been shown whether the carbide of iron is actually deposited at a high temperature due merely to an excessive concentration at the boundary surfaces or whether precipitation is caused by the alteration of the saturation value on cooling. That it is possible to have excessive adsorption and so overstepping the solubility of the solute has been shown by Ramsden (Zeit.phys.Chem. 47, 336) for solutions of soap, albumen, and certain dyestuffs. It has

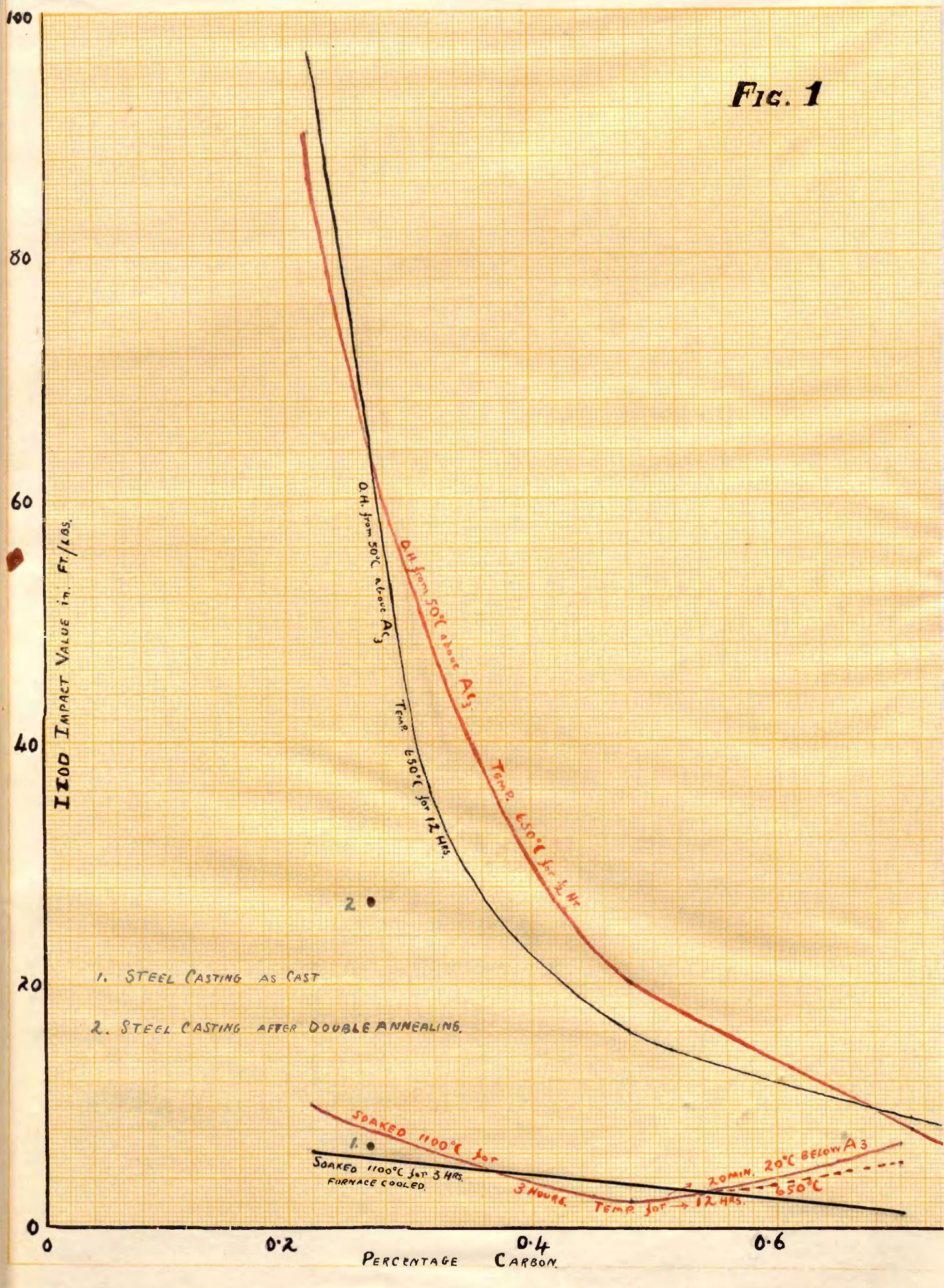
also/

also been shown that if two solutes are present, that which lowers the surface tension to the greater degree is the one which forms the surface film. Of course the above equation cannot be applied to cases in which excessive adsorption resulting in precipitation, occurs.

Although it is not possible, at present, to apply thermodynamical considerations to metallurgical problems of this kind yet, in a qualitative way this view of the subject is beginning to receive attention. Giolitti has used it to account for the influence of manganese on liquid steel (J.of Iron and Steel Inst. 1923, No.2). It can be applied to account for the carbide of iron films in the low carbide steels and also to explain the results of Andrew on the effects of phosphorus on impact brittleness (N.E. Coast Inst. Eng. and Ship. 1920).

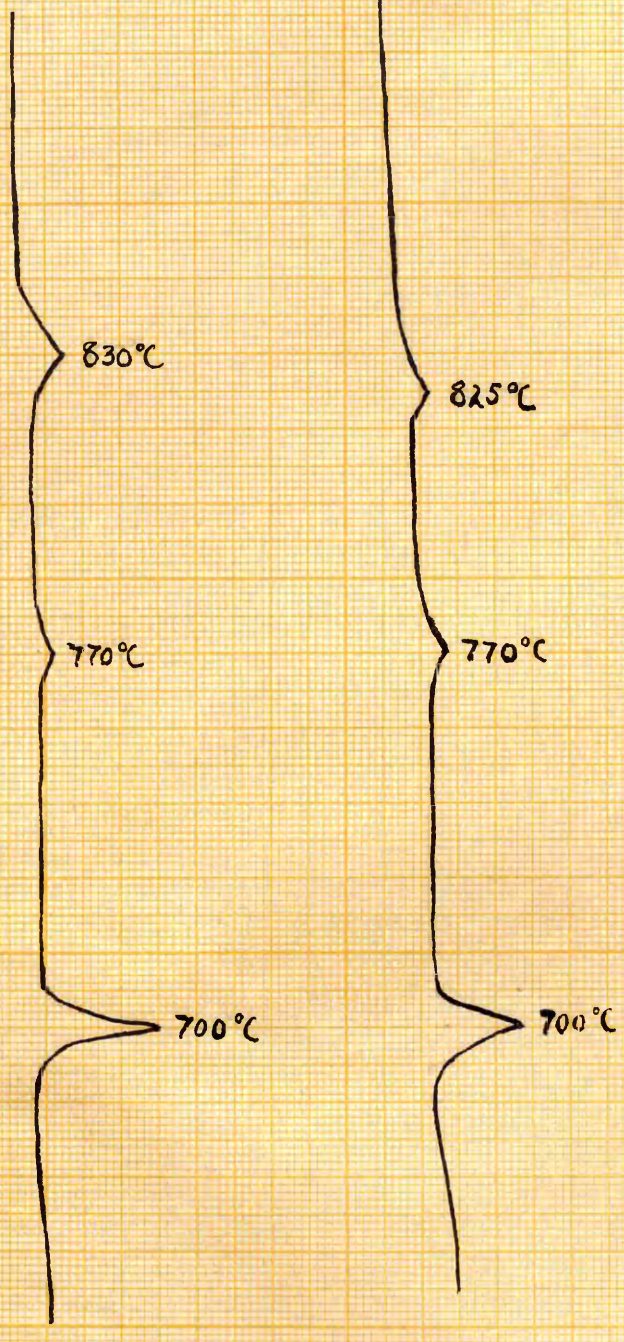
The formation of films of the carbide of iron at the grain boundaries of the low carbon steels depends upon two factors. First it is necessary for the dissociation of the complex carbide molecule; then the simple carbide molecule, or, more probably, the carbon atom diffuses to the grain boundaries at which it increases in concentration. Consequently there exists here a chain of carbon atoms attached to the iron atoms and, when separation takes place, a film of carbide of iron exists where the original high temperature boundary existed. Prolonged soaking at a high temperature brings about these results. In this way a large number of the irregular results obtained in impact testing can be very satisfactorily accounted for.

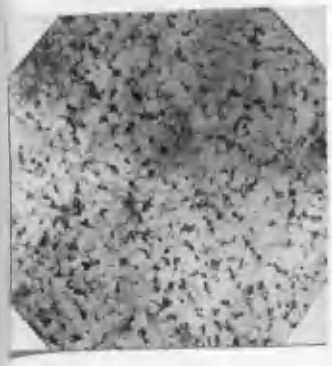
# FIG. 1


100
80
60
40
20
0
IZOD IMPACT VALUE in. FT./LBS.
0
0·2
0·4
0·6
PERCENTAGE CARBON.
O.H. from 50°C above $A_{C_3}$
O.H. from 50°C above $A_{r_3}$
TEMP. 650°C for 12 HRS.
TEMP. 650°C for ½ HR.
2
1. STEEL CASTING AS CAST
2. STEEL CASTING AFTER DOUBLE ANNEALING.
SOAKED 1100°C for
1
SOAKED 1100°C for 3 HRS.
FURNACE COOLED.
3 HOURS
TEMP for → 12 HRS.
20 MIN.
20°C BELOW $A_3$
650°C

Soaked at 1000°C
for 2 hours.

**Fig. 2.**





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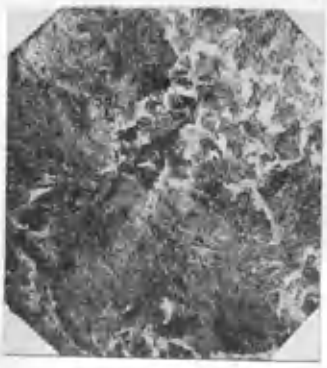
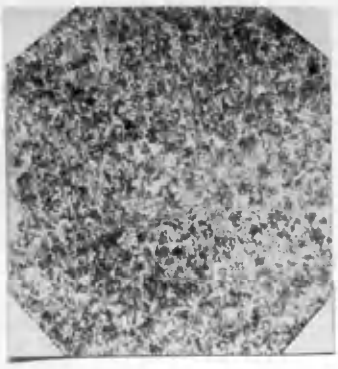
MICRO N°2 X75



MICRO N°3 X75

MICRO. N°4 X75

MICRO N°5 X 75



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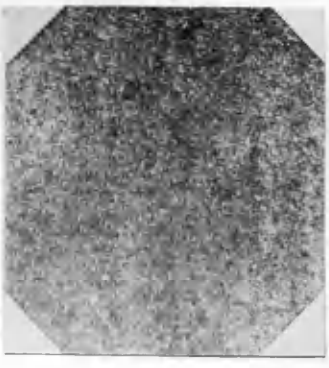

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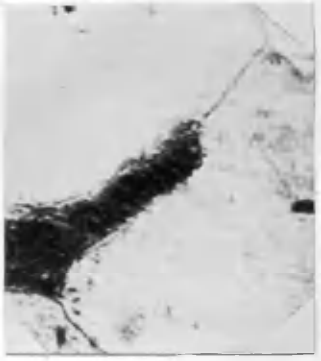

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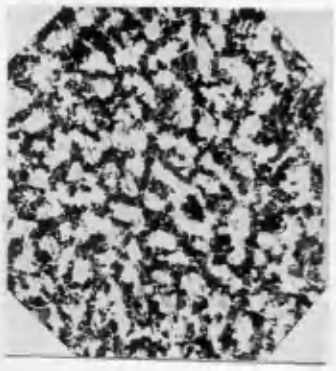

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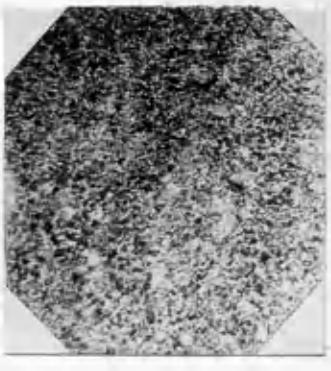

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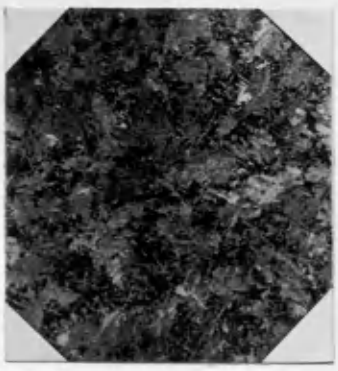
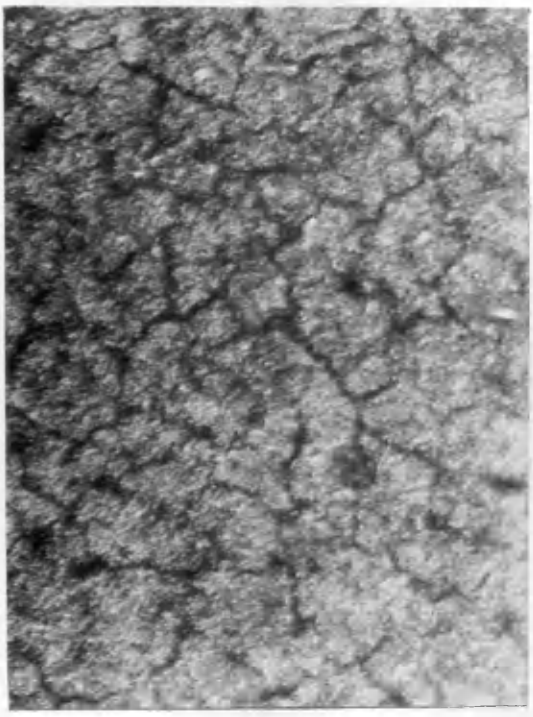


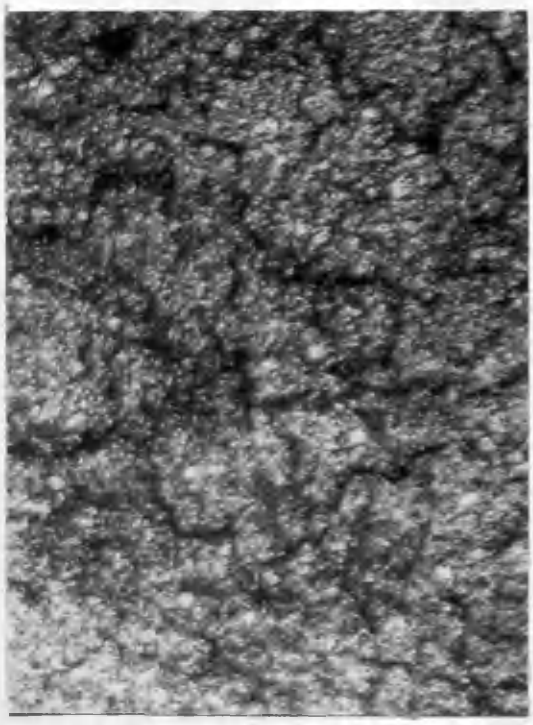
MICRO. N°11 X75

Etching Reagent $HNO_3$ in Alcohol

MICRO N° 12 X 600
Etched Alkaline Sodium Picrate



MICRO N° 13 X 85
Etched with Iodine



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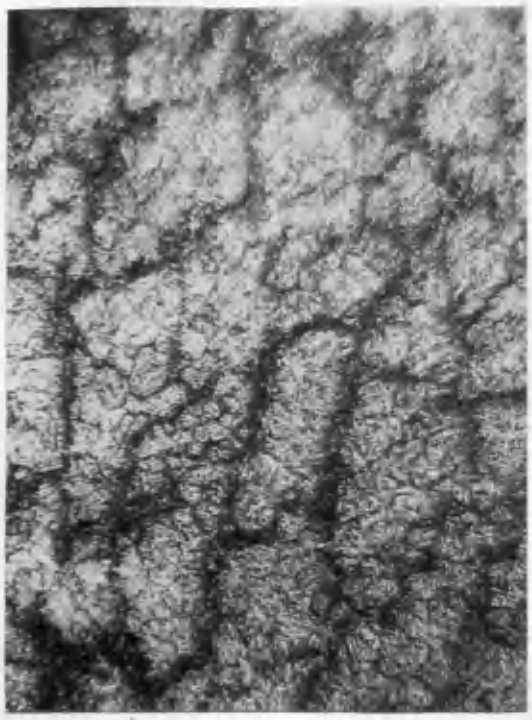

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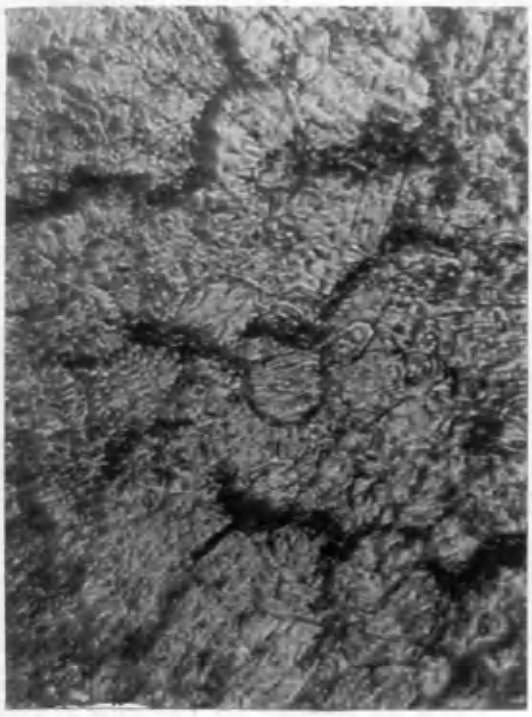

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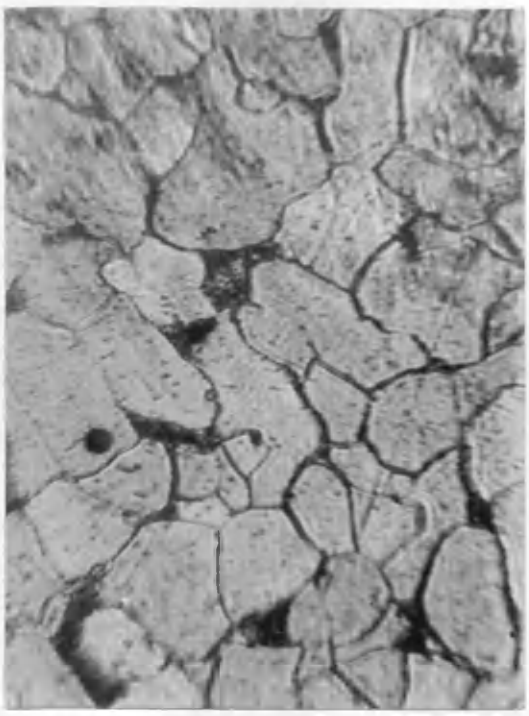
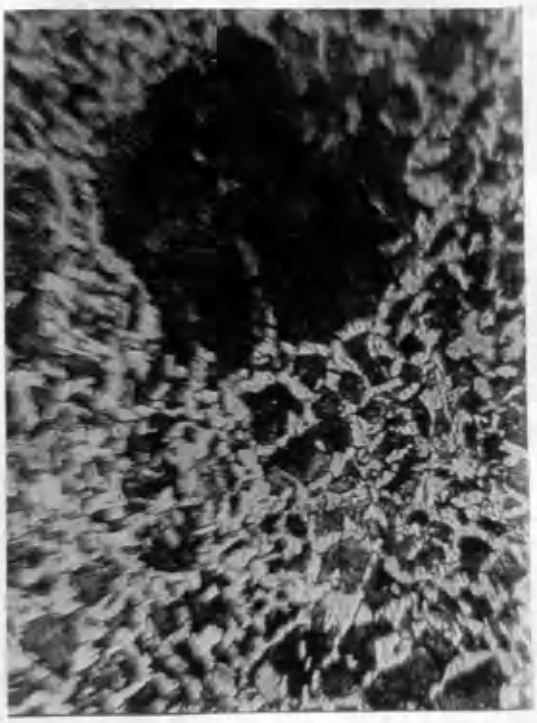


MICRO. N°17 X1300
Etched with $HNO_3$ in Alcohol

MICRO N°18 X120
Etched with $HNO_3$ in Alcohol



MICRO N°19
Etched with $HNO_3$ in Alcohol

Book 11.

Contents.

# A Study of the Constitution of the Copper-Zinc Alloys.

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The copper-zinc alloys have received much attention from research workers, no doubt because of the industrial importance of the copper rich alloys. Further interest has been added to this system by the rediscovery in 1911 by Carpenter and Edwards (1) of the critical point at 470°C. (previous found by Roberts-Austen (2)) in alloys containing the beta constituent. Their interpretation of this change point was that the beta constituent broke down into the adjacent phases, alpha and gamma, thus being in the nature of a eutectoid change.

In 1914 Hudson (3) put forward very strong evidence in favour of the view that the change at 470°C. was of a polymorphic nature, the beta constituent changing into what he termed beta dash.

Isamai (4) at a later date pointed out that 470°C. change, which he found took place over a range of temperature, was of a non-allotropic nature and of the same type as the $A_2$ change in iron as expressed by Honda (5).

In view of the great divergence of opinion in regard to the nature of the 470°C. change in the beta constituent it was decided to commence investigations at the copper end of the series, paying particular attention to the beta constituent, and, if results warranted it, to extend the investigation to comprise alloys of composition varying right across the system.

## Electrolytic Potential.

The method of study selected was Electrolytic Potential measurements.

## Theoretical.

The theoretical aspect of this subject has received much consideration from physicists with the result that it can be used with a fair amount of confidence. Kelvin and also Helmholz showed that the type of reaction involved in the development/

development of an electrolytic potential belonged to the Second Law of Thermodynamics from which the general equation of

$E - U = T\frac{dE}{dT}$ is derived where E = the external work done by the current, and U = the heat of reaction. This equation has been shown to hold in many instances, but it is of no real value as integration is necessary before the electromotive force can be obtained from thermal data.

Nernst (6) furthered the theoretical aspect of the subject by treating the matter from the ionic standpoint. His treatment not only simplified theoretical calculations, but also gave a picture of the mechanism of electrolytic potential phenomena. According to Nernst, all metals possess the property which he called "solution pressure," which tends to drive the positively charged ions of the metal into the surrounding solution. If the surrounding solution already contains ions of the same metal then these ions in the solution exert an opposing force, for these ions having an osmotic pressure will tend to be deposited at the surface of the metal giving a back e.m.f. When there are just as many ions leaving the metal (or electrode) under the influence of the "solution pressure" as there are being deposited upon it by the effect of the osmotic pressure, then there will be a state of equilibrium set up, and consequently the electro-motive force between the electrode and the solution will be zero. In all other cases there will be an electro-motive force between the electrode and the solution. Ions will pass either from the electrode to the solution resulting in the electrode being negatively charged with respect to the solution, or, conversely, from the solution to the electrode when the latter will become positively charged. In either case only a very few ions will flow before equilibrium is established between the electrode with its electrical field (that is the positively or negatively charged electrode) and the solution.

From the above, it will be seen that it is not difficult to derive an equation, based upon the 2nd Law of Thermodynamics similar to that obtained for osmotic pressure. This equation was derived by Nernst and is as follows:-

$$E = \frac{R \cdot T \cdot}{n \cdot F} \log_e \frac{p}{P}$$

where n = valency of the ion

p = osmotic pressure

and P = solution pressure

or expressing p and P as concentration factors.

$$E = \frac{R \cdot T \cdot}{n \cdot F \cdot} \log_e \frac{c}{C}$$

where c = concentration of metallic ions in solution.

and C corresponds to P in above equation.

As will be observed from the above equations P and C have no real physical meaning. If a compound cell is used in which the electrodes are of the same meterial,then, in the algebraic sum of the "cell" values, the P or C will cancel out. For example, if an electrode of silver is dipping into $\frac{N}{1}$ $AgNO_3$ in one half cell and another silver electrode is dipping into $\frac{N}{10}$ $AgNO_3$ in another half cell then the total E.M.F. from the cell will be

$E = \frac{RT}{nf} \log_e \frac{C}{c_1} + \frac{RT}{nF} \log_e \frac{c^2}{C}$ when $c_1$ and $c_2$ are the ionic concentrations in the respective solutions and C is the ionic concentration of the electrode, or

$E = \frac{RT}{nF} \log_e \frac{c_2}{c_1}$. In cases where the electrodes are dissimilar then the more complex condition prevails but matters can be simplified by keeping one half cell a constant in any series of measurements. For this purpose the Hydrogen cell or the Calomel cell can be utilised. Although the value of both of these cells is fairly accurately known yet the indeterminate and physically meaningless quantity of "solution pressure" still remains. It is obviously this factor in the equation which will determine the type of curve obtained in alloy measurements in which the electrolyte is kept a constant.

In/

In the study of the constitution of alloys the constituents of the alloy may exist in the fundamental states, namely (a) the constituents may be completely insoluble in each other and so form a mechanical mixture, (b) the constituents may be mutually soluble in each other when a solid solution results and (c) the constituents may form an intermetallic compound when the chemical identity of each is lost. The typical electrolytic potential curves for the three cases may easily be derived. For case (a) it is the constituent of the mixture which has the greatest "solution pressure" in the electrolyte that is registered in the P.D. value, that is, the more active or less noble metal under the conditions of the experiment. Laurie (7) showed this in a very pretty manner by taking a piece of copper and embedding in its surface a very small piece of zinc and measuring the P.D. ~~xxxxxx x xxxxxxx~~ in $Cu_2I_2$ solution. The mere speck of zinc registered its electrolytic potential, not the large mass of copper as might have been expected. Consequently in the case where we have two insoluble phases so long as these persist with the changing composition then the electrolytic potential throughout the whole system will be invariable. In case (b) a different state of affairs exists. In a solid solution it would appear from X-ray studies and other considerations, that, at least in the majority of cases, if not in all, the solute atoms take up a position in the lattice of the solvent atoms (8). As the amount of solute is increased the concentration of the solvent will be decreased. This will result in the concentration-electrolytic potential curve being logarithmic in form. Moreover any alloy in a series of completely miscible binary alloys must have an electrolytic potential less than that of the more active constituent. Case (c) presents a state of affairs in which the result cannot be predicted. If the compound can exist as such in solution in the electrolyte then it will exert its own "solution pressure," and its presence in a series of alloys

will/

will be marked by a break in the concentration-electrolytic potential curve.

Whilst the views of Nernst serve as a background upon which to build some crude type of mental picture of the mechanism of electrolytic potential it has been fairly conclusively shown by Rideal (9) that it lacks true meaning in spite of agreement between calculated and observed results. Richardson from thermoionic emission and electrical conductivity determinations has shown that the number of free electrons per ~~cent~~ unit. volume is practically the same for all metals. He has also shown, as has Milliken and others, that the electron affinity is a characteristic of a metal and Rideal (9) has shown that there is a distinct relationship between the electron affinity and the electrolytic potential. Over against these views upon the subject, Butler (10) has treated the subject of electrolytic potential from the kenetic standpoint and finds good agreement with Nernst's views.

Although the true meaning of electrolytic potential is still unknown, yet with care in interpretation, the results of an investigation, based upon the earlier views of Nernst, are capable of yielding valuable information on the constitution of alloys.

Not only is a potential difference developed at the metal/liquid junction but a similar state of affairs results at all liquid/liquid junctions. Generally the latter is of a very much smaller order of magnitude than the former but where absolute results are required this must be taken into consideration. In the constitutional study of alloys this factor is constant and can be neglected. Moreover its effect can be minimised by employing an intermediate liquid such as a solution of ammonium nitrate, or potassium chloride. Exactly in what manner this intermediate solution functions in reducing or annulling the liquid/liquid potential is not, however,/

however, clearly understood.

The influence of temperature upon the electrolytic potential difference is the remaining point to be considered. According to the Nernst equation temperature plays an important part in determinations of this kind. Meyer (11) and also Richards and Daniell (12) found that variation in temperature did affect the potential difference values but the variation was not of the order of magnitude expected from the equation. Actually in the experimental investigation it was found that the slight variation in room temperature made no difference to the electrolytic potential values. Rideal(9) even goes so far as to say that the electrolytic pressure is apparently independent of its temperature.

Previous Work. Although the P.D. values for the Copper-Zinc system of alloys have been determined by many workers yet the results obtained show a great lack of agreement. This is not surprising when the complexity of the phenomena involved is borne in mind. Moreover little or no attention seems to have been given to the state of the surface of the alloys used, and yet this is of vital importance. Frequently no mention is made of the treatment of the alloy, whether it is in the cast or annealed states. The choice of the electrolyte received some attention from some workers whilst others showed a total lack of consideration of this most important factor.

Probably the oldest work in this field is that of Trowbridge and Stevens, (13). The object of their investigation was "to note the variation of E.M.F. in different alloys of the same metals and to deduce if possible, some general law which governs the variation." They used as electrodes, lead and the alloy under investigation and fresh pond water as an electrolyte but did not get satisfying results. Using distilled water, acidulated with sulphuric acid, they obtained better results, but, as far as the Cu-Zn alloys are concerned, the results were far/

far from those found by later workers. Their deduction, that the E.M.F. varied as the most soluble metal, is wrong. The figures which they obtained using acidulated water as electrolyte are given in Table I.

In 1888 Laurie (7) published the results of his work on Electrode Potential measurements of alloys which included the Copper-zinc series. His work was very much superior to that of Trowbridge and Stevens. He used a solution of a salt of the more negative metal as electrolyte but the state of the electrode received no attention and theconcentration of the electrolyte did not receive special attention. He pointed out that the compound in the Cu-Zn series was $CuZn_2$. His results are given in Table II. using a $Cu_2I_2$ cell.

In a paper entitled "Beitrag zu Kenntnis der Metallegierungen" by M.Herschkowitsch (14) (Zeit für Physik. Chemie. 27. 123. 1898) is given a full account of the electrode potential measurements and a brief account of the theory of the subject. From his determinations of the CuZn series he deduced that there is a compound of the formula $CuZn_2$. He used a salt of the less noble metal as electrolyte, choosing $ZnSO_4$ and measured the P.D. of the alloys against Zinc this being the more active metal. Moreover he used an electrolyte of a fixed strength, namely a normal solution. The agreement between his four sets of determinations is not good. For example an Alloy containing 39.3 "molecular percentage" of zinc gave results as follows:- 1000.0; 1030.0; 848.0; 976.0; millivolts. At the Zinc rich end of the series agreement was better. One series of his results is given in Table III.

Undoubtedly the best work on the P.D. measurements of the CuZn series of alloys is that of N.Puschen. His work was published in the Berichte des St.Peter. Polytech. Institute in in 1906 and in Journ. Russ. chem. Gesell in 1907. A translation of it appears in the Zeitschrift für Anorganische chemie in 1908. (15) Like Herschkowitsch he used N/1 $ZnSO_4$ as the electrolyte/

electrolyte and measured the P.D. against Zinc but he made a much more systematic study of the subject. Between 13 and 15 atomic % of copper he found a sudden fall in P.D. and this he attributed to the phase $Zn_6Cu$ and he assumed that a compound formed between these percentages. It is worthy of note that he found an increased P.D. as result of adding copper to zinc a maximum being attained at about 12 atomic per cent of copper. He made no mention of this interesting point however. At 33 atomic per cent. of copper he found another fall in P.D. but of a very much more pronounced nature. This drop corresponds with the composition $Cu\ Zn_2$ and this had already been noted by Laurie and Herschkowitsch. At about 53 atomic per cent. and at 67 atomic per cent. he noted a further fall in the P.D. and this, in turn, he attributed to the appearance of new compounds to which he assigned the formulae Cu Zn and $Cu_2Zn$. Table IV shows his results and in the last column is shown the e.m.f. values between N/1 $Zn\ SO_4$ and the various alloys, calculated from his data.

Experimental:- In view of the great differences in the results obtained by earlier workers it seemed very essential that more attention should be given to the various points discussed in connection with the theory of the subject, namely the question of a suitable electrolyte and also of the condition of the surface of the specimen.

For the purpose of a preliminary survey three alloys of copper content 70%, 52% and 40% respectively were made from pure electrolytic copper and pure spelter. The alloys were in the alpha, beta and gamma respectively. The importance of uniform and sound alloys being realised, the following method was adopted. A piece of thin, clear silica tubing, 2 millimetres in bore and 10 inches long was attached to an evacuated suction flask, there being a clip in the rubber tubing between the flask and the silica tube. The

silica/

silica tube was heated and then dipped into the molten alloy, the clip released. The metal was drawn into the tube for a distance of about six inches. The alloys were found to be sound and uniform. Pieces of the alloys were set in glass tubing of greater bore than the diameter of the specimens, being fixed at the lower end with the aid of plastic wax. The annular space between the specimen and the glass tube was filled with mercury which served as a means of connecting the alloy to the copper wire leading to the potentiometer.

A Tinsley potentiometer was used for the measurement of the e.m.f.. Half cells of the standard Ostwald pattern were used. In the early experiments pure copper was used as the reference electrode and the electrode in the other half cell was either the alpha, beta or gamma alloy. The reference electrode was fitted up in the manner already described. The e.m.f. of the one alloy against the other was also determined experimentally.

The choice of a suitable electrolyte presented a problem of considerable difficulty. Theoretically it is necessary that ionic equilibrium be obtained, From Kohlrausch's equivalent conductivity tables the ionic concentration of Cu $SO_4$ and Zn $SO_4$ solutions can be calculated on the assumption that dissociation is complete at 0.0001 molar concentration. These are given in Table V. However the method of determining the ionic concentration of the various alloys presents another problem. Tamman in his "Lehrbuch der Metallographie" has suggested that the ionic concentration of the more noble metal should be increased until no more of the solid solution of the more noble metal is precipitated from the electrolyte. The sensitivity of this method seems doubtful from the experimental work carried out and did not give practicable results.

The first electrolyte to be used was N/1000 Cu $SO_4$ but, although/

although very consistent results were obtained for the alpha and beta alloys, the sensitivity was low, 0.033 volts on the bridge only giving a scale deflection of 2 millimetres. The addition of 0.1% $H_2SO_4$ to the electrolyte was tried but the results were unsatisfactory. They varied rapidly, due, no doubt, to polarisation effects. KCl was added to the electrolyte in place of $H_2SO_4$. This was chosen because it is a very good ion carrier and the K and Cl ions travel at about equal speeds. This greatly improved the sensitivity, but, as was expected, varying the KCl greatly changed the results. Had pure metals only been used this could have been allowed for but when dealing with complex alloys and the composition and constitution of these varying from alloy to alloy this would be an added variable to a very difficult problem. A solution of cupric chloride was next tried as an electrolyte but with no better result. Copper ammonium chloride and also copper ammonium sulphate were each tried in turn and rejected. N/1000 Zn $SO_4$ was also tried but was much inferior to N/1000 $CuSO_4$. The results could not be repeated and the sensitivity was only 0.04 volts to 2 millimetres on the scale. An electrolyte composed of N/1 $CuSO_4$ and N/1 Zn $SO_4$ mixed in the proportion to give the Cu and Zn contents of the electrolyte the same as that in the alloy under examination. As before sensitivity was the stumbling block. The results obtained were good as is shown by the following figures for Cu in N/1000 $CuSO_4$ and the alpha alloy in an electrolyte of 64% N/1 $CuSO_4$ and 36% N/1 $ZnSO_4$:- 0.0265, 0.0265 and 0.0265, the last reading being taken 3 minutes after the insertion of the alloy in the mixed electrolyte. After further trials with various concentrations of $CuSO_4$ it was decided to use N/1 Cu $SO_4$, this being found very much more sensitive than the other concentrations. Moreover the results could be repeated with

an/

an accuracy of 0.0005 volts.

The series of alloys shown in Table VI was prepared in a manner similar to that already described. These alloys, however, are not mounted in glass tubes, it being considered that the Hg junction introduced an unnecessary complication. The copper wire was fixed to the end of the thin alloy rod by a binding screw, and the rod mounted in a small rubber cork. About 1 inch of the rod passed through the cork and dipped into the electrolyte. Using an approximately N/1 $CuSO_4$ solution as electrolyte and a copper rod as the standard against which the alloys were measured, the following interesting results obtained.

| Cast Mark. | Actual E.M.F. on potentiometer. | Sign of copper electrode. |
|---|---|---|
| A | .0235 | negative |
| B | .0220 | negative |
| C | .0055 | positive |
| D | .047 | positive |
| E | .042 | positive |

Only the copper rich alloys were dealt with during the early stages of this work. It was found very difficult at this time to get anything approaching consistent results with the gamma alloys. The remarkable point about the above figures is the change in sign between B and C and that B is greater than A. This change will be discussed at a later stage.

Although consistent results had been obtained for the copper rich alloys and these had been repeated on three/

three independent days yet it was realised that trouble might have arisen from the use of $Cu/N/1CuSO_4$ as a standard cell due to the difficulty of maintaining the state of the surface of the copper standard in a perfectly constant condition. In fact, this trouble did arise in the course of a few weeks so that measurement against copper was abandoned. Earlier investigators had used $Zn/N/1ZnSO_4$ for the standard half of the cell. But this is open to the same objection. It seemed much more satisfactory to use either of the recognised standard cells, that is, either the Hydrogen electrode cell, or the calomel cell as a standard. The calomel cell was selected and this was used throughout the remainder of the work.

A simple experiment was carried out to see how far strain might interfere with the e.m.f. obtained. For this purpose a piece of the alloy B (81.4% Cu) containing 81.4% Cu was selected. The e.m.f. of this alloy in an electrolyte of 81.4%N/1000 $CuSO_4$ and 18.6%N/1000 $Zn\ SO_4$ containing N/1KCl was measured against the calomel cell. The value of the combined cell was .198 volts. Straining the alloy very slightly by lightly hammering it, preparing the surface as before by carefully cleaning it with 000 French emery paper and testing it in a similar electrolyte, a result of .213 volts was obtained for the combined cell. This is in agreement with the work of Merica (16) who also found a slight increase in the e.m.f. of alloys due to cold work.

All specimens were used in the annealed state and had their surface prepared in the same manner each specimen being finished with 000 French emery. With this precaution no serious difficulty was experienced in obtaining results which could be repeated.

The problem of the influence of the connecting of the two half cells upon the resulting e.m.f. had still to be considered./

considered. For this purpose a N/1 KCl solution was used as the speed of the K and Cl ions are nearly the same and this salt is largely dissociated in solution. $NH_4Cl$ would seem almost as good from the foregoing reasons but as N/1 KCl is used in the standard calomel cell it was preferred. The magnitude of the electrolytic potential due to diffusion at the liquid/liquid junctions was a matter of some importance. It had already been found when investigating the problem of a suitable electrolyte that the concentration of the KCl added to the electrolyte had considerable effect on the resulting e.m.f.. This may be seen from the following figures:-

Type of combination cell $Hg/\ Hg_2Cl_2$ N/1 KCl / N/1 KCl / N/1 $CuSO_4$ + reqd. KCl / Cu

| Sign of calomel cell. | Conc. of KCl present in electrolyte. | E.m.f. of total cell in Volts. |
|---|---|---|
| negative | none | .025 |
| negative | N/1000 | .006 |
| negative | N/100 | .011 |
| positive | N/10 | .037 |

This effect, of course, could be largely eliminated by keeping a constant strength of KCl in the connecting cell though its influence on the final result would be unknown. In order to arrive at some idea of this value the following experiments were performed. A copper electrode was carefully prepated as previously described, and the e.m.f. of this electrode in an electrolyte of (a) N/1 KCl, (b) N/1 $CuSO_4$ and (c) a mixed electrolyte of N/1 KCl and N/1 $CuSO_4$ against the calomel cell was determined.

These experiments gave results as follows:-

| | | E.M.F. of total cell. | Sign of calomel cell. |
|---|---|---|---|
| (a) | $Hg/\underset{N/1\ KCl}{Hg_2Cl_1} / N/1\ KCl/ N/1\ KCl/Cu$ | 0.153 volts. | positive |
| (b) | $Hg/\underset{N/1\ KCl}{Hg_2Cl_2} / N/1\ KCl/N/1 CuSo_4/Cu$ | 0.025 volts. | negative. |
| (c) | $Hg/\underset{N/1KCl}{Hg_2Cl_2}/N/1\ KCl/ N/1KCl/ Cu$ $/ N/1\ CuSO_4$ | 0.105 volts. | positive |

Although in the first case there was no diffusion potential coming into play and in the second case the diffusion potential of $N/1KCl/N/1\ CuSO_4$ existed, there was no evident means of obtaining this quantity from case (c). It is not correct to assume that the difference (.153-.025) and 0.105, that is 0.128-.105, = 0.023 was due to the difference of concentration of $N/1CuSO_4$ in the case (c) from Case (b). KCl is dissociated to extent 0.72 in N/1 solution whereas N/1 $CuSO_4$ is only dissociated to extent of 0.2275 which means that Cu/N/1 KCl is more active than $Cu/N/1\ CuSO_4$.

As nothing definite could be obtained from these figures and yet it looked as if this matter might be of considerable importance a few more experiments were carried out. The solution in the connecting cell was replaced by N/1 $NH_4Cl$ thus changing one of the ions in order to see if any considerable difference would accrue. However no difference was observed both combinations giving the value for $Cu/CuSO_4$ as o.585 volts assuming the calomel cell to be 0.560 volts. The actual reading for the combined cell was 0.025 volts in each case. Although this did not disprove the importance of diffusion potential, the results were encouraging.

Resort was now made to theoretical calculation. Here again as it was two binary solutions which were being considered and as both univalent and bi-valent ions were present, the problem became very involved. An approximation may be obtained however from the following equation

$$\mathcal{E} = \frac{RT}{F} \log \frac{l_c + l_a}{l'_c + l'_a}$$

where $l_c$ and $l_a$ are the ionic conductivies of the ions of one electrolyte and $l'_c$ and $l'_a$ are conductivies of the other.

Taking $l_c = \dot{K} = 64.9$

$l_a = \bar{c}l = 65.4$

$l'_c = \dot{C}u = 45.9$

$l'_a = \bar{S}O_4 = 67.2$

it is found that E = .004 volts.

Thus the diffusion potential is of a small order in comparison with the electrolytic potential of $Cu/CuSO_4$ N/1.

The influence of temperature was not determined. All determinations were carried out at room temperature. During the months while these preliminary investigations were being conducted, no evidence of temperature being an important factor was indicated. From the Nernst equation it would be naturally concluded that this factor is of importance although in his paper dealing with the "Mechanism of the Reversible Electrode" Rideal (9) states there is an apparent independence of the electrolytic solution pressure of a metal with respect to temperature.

The P.D. value for all the specimens shown in Table VI was now determined making use of the information gained by the preliminary experiments. The electrolyte used was N/1 $CuSO_4$, the calomel cell being used as the other half-cell and N/1 KCl as the solution for reducing diffusion potential. The electrolyte was renewed in the cell after each determination and the N/1KCl was frequently replaced. Each determination was made many times. No difficulty was experienced in repeating the values for the alloys rich in copper but as the gamma compound was approached it became increasingly difficult to obtain satisfactory results. The results are given in Table VII.

It was deemed advisable to repeat the above experiments using N/1 $ZnSO_4$ as electrolyte in place of N/1 $CuSO_4$. In this case it was very difficult to obtain satisfactory results with the copper rich alloys but for alloys beyond the gamma range consistent results were obtained. The results are stated in tabular form in Table VIII.

The results obtained were considered sufficiently promising to make it worth while making a more complete set of alloys and determining the electrolytic potentials for the whole series. Consequently the alloys shown in Table IX were prepared. In this case, however, these were not made by drawing into thin quartz tubing, this method proving too expensive. On this occasion the alloy was cast into small moulds, $\frac{3}{4}$ inch x $\frac{3}{4}$ inch x 3 inch long. The small ingots were packed in charcoal and carefully annealed until all "cast structure" had disappeared as revealed by microscopic examination. From the solid centre portion of these ingots were turned small plugs $\frac{3}{4}$ inch long by 3/8 inch in diameter. Into the centre of one end of each plug a small hole was drilled into which fitted a copper rod with a tapered point. To this copper rod was fixed the copper wire leading to the potentiometer. This method of mounting was found very convenient as it necessitated only the changing of the plug.

The results obtained for this series of alloys in N/1 $CuSO_4$ and N/1 $ZnSO_4$ electrolytes are given in tables Nos.X and XI respectively and along these with the/

the results obtained from the first series of alloys, are incorporated in graphical form in Figure I.

The P.D. values for the second series of alloys were also determined in an electrolyte composed of a mixture of N/1$CuSO_4$ and N/1$ZnSO_4$. The electrolyte was made up so as to contain the same amount of Cu and Zn as the alloy whose P.D. was to be determined. This would not give quite true ionic concentrations as it has already been shown that $ZnSO_4$ and $CuSO_4$ do not dissociate to the same degree in N/1 solutions although very nearly so. The difficulty lies in knowing how the alloys of Cu and Zn behave in regard to ionic concentration at the surface. In the early work the influence of variation of composition of the electrolyte upon the e.m.f. was determined and the following data obtained:-

| Sign of Calomel cell. | Composition of electrolyte + KCl | | Alloy. | Total c.m.f. |
|---|---|---|---|---|
| | $CuSO_4$ | $ZnSO_4$ | | |
| positive | 95 | 5 | No.B (81.4%Cu) | 0.198 |
| positive | 90 | 10 | ditto | 0.198 |
| positive | 85 | 15 | ditto | 0.197 |
| positive | 80 | 20 | ditto | 0.197 |
| positive | 75 | 25 | ditto | 0.197 |
| positive | 70 | 30 | ditto | 0.199 |
| positive | 60 | 40 | ditto | 0.202 |
| positive | 50 | 50 | ditto | 0.205 |

This shows that, at least for the copper rich alloys, very little difference was obtained over a wide range of electrolyte concentration. In this connection it is interesting to note that A.E.Taylor (17) in his study of irreversible cells stated that the e.m.f. of the cell $Zn/ZnSO_4/CuSO_4/Cu$ was independent of the absolute concentration of the Zn and Cu sulphates. It is also of interest to observe that in the same paper he gave the values of Copper to Normal $CuSO_4$ as - 0.585 volts and Zinc to Normal $ZnSO_4$ as 0.524 volts, results which are in very good agreement with the above experiments (Tables X and XI).

In table XII are given the results observed using the mixed electrolyte. It is worthy of mention that for the copper rich alloys the results are in very close agreement with those obtained in the N/1 $CuSO_4$ electrolyte and similarly those at the Zinc end of the series are in agreement with the data derived from the N/1 $ZnSO_4$ electrolyte.

The alloys in the centre of the series containing much gamma gave much trouble both in N/1 $CuSO_4$ and in N/1 $ZnSO_4$ solutions. It was found difficult to repeat the results and obtain consistent results. This, no doubt, was due to the difficulty of preparing a satisfactory surface. Latterly fractured surfaces were used, the remainder of the surface of the specimen, except the clean fractured portion, being covered with vaseline. This procedure gave better results. Finally, the result obtained on the immediate immersion of the specimen was taken as the true reading. By this device tolerable agreement between successive determinations was obtained.

A short study of the effect of heat treatment of alloys around the beta range of composition was made. For this purpose a series of specimens were heated to 600°C. soaked at this temperature for 20minutes and then quenched in water. The surface of each was carefully prepared and the P.D. determined/

determined in N/1 $CuSO_4$. The data so obtained is given in table XIII. It is significant that quenching increases the P.D. value of alloy to N/1 $CuSO_4$ within the beta range but has no effect on the alpha solid solution.

Consideration of results.

The results are shown in graphical form in Figure 1. At the outset it is worthy of remark that Puschin's[15] curve follows the same general outlet as obtained in the present work. The marked drop in the curve at approximately 33% of Cu distinctly points to the fact that $Cu_2Zn_3$ is not the most active compound in the Cu-Zn series; in fact there is no evidence of its existence in this property-curve. Herschkowitsch and Puschin both placed the intermetallic compound at 32.8 Cu and assign the formula $CuZn_2$ to the compound. The present work is in good agreement with this view. Westgren and Phragmen (18) (Phil. Mag. Vol.50, 295, p.311) have tentatively suggested that $Cu_4Zn_9$ is the composition of the compound in this region of the Cu-Zn series from a study of X-ray diffraction patterns of this series of alloys. From Figure 1 it is difficult to assign any very definite composition to the compound as the sharp change in direction of the curve would appear to refer to the limits of the compound phase rather than signifying its particular composition. In this range of alloys better results were obtained by using N/1 $ZnSO_4$ solution. The results are shown in Figure 2.

It is significant that the copper rich alloys in N/1 ZnSO4 gave a lower value for the P.D. than when immersed in N/1 $CuSO_4$. That the results in the different electrolytes would not be the same would be expected but it is not so obvious why the amount of this difference is practically the same at the two ends of the series. Still more significant is that fact that within the range of the alpha solid solution the curve for N/1 $CuSO_4$ and for the mixed electrolyte of N/1 $CuSO_4$ and N/1 $ZnSO_4$ practically superimpose upon each other. The agreement for the eta solid solution/

solution is not quite so good though of the same order being much better than with N/1 $CuSO_4$ electrolyte. This fact points very strongly to the view that, in the alpha solid solution range, Copper is the active constituent and hence the good results with N/1 $CuSO_4$ electrolyte. The Zinc in this range is not the active constituent as was assumed by all earlier investigators. Similarly at the eta-solid solution end, Zinc is the active constituent.

The results obtained for the Copper rich alloys with N/1 $CuSO_4$ electrolyte are shown on a larger scale in Figure 3. It is very remarkable as mentioned earlier in the paper that with additions of Zinc to Copper up to about 10% of Zinc the curve shows a decided rise. In the earlier work it was found that strain raised the e.m.f. Undoubtedly the cause of this increase in e.m.f. is due to the added Zinc distorting the space lattice of the Copper and so causing strain. It is most remarkable that this effect should cease at approximately 10% Zn. Ingalls (19) (Inst. Metals, 1925, No.2, 34) has observed a change at about 9% Zn in the High Temperature-Tensile Curves and attributed this change to space lattice considerations. He says "It would appear that the fundamental lattice of copper is maintained up to about 9 per cent. of zinc, after which there is a change, giving a lattice which may be termed alpha, which is maintained until the appearance of the beta lattice." Whilst not in entire agreement with Ingalls as to his explanation it does seem that there is a change taking place up to 10% Zn and then a new set of conditions prevail. From 10% Zn to 36.5% Zn the curve is logarithmic in form. That this curve is truly logarithmic was proved by drawing the log curve whence a straight line was obtained as shown in Figure 4. From 10% Zn up to 36.5% Zn the curve follows that required by theory for a true solid solution. In this portion of the curve the Zn merely acts as a dilutent. Hence in the equation $E = \frac{RT}{nf} \log \frac{C}{C_1}$, where C = ionic concentration of copper ions in the electrolyte and $C_1$ = ionic concentration of copper ions in alloy, $C_1$ is the only/

only variable and hence resulting equation is logarithmic.

From 36.5% Zinc to 57.87% Zn, however, the curve is very far from logarithmic as is seen from Figure 5 in which the log values are plotted. Whereas in the alpha range there exists true solid solutions conditions, in the beta range some other state-exists. Even in the case of the quenched alloys matters are not simplified. Here again in the alpha range the quenched values are logarithmic being the same as the annealed values. But in the beta range the values of the e.m.f. are increased by quenching. This curve neither obeys the form required for solid solution conditions nor for the eutectiferous series.

In Figure 6 the results for the zinc rich alloys in N/1 $ZnSO_4$ are recorded graphically on a large scale. Here again the addition of Copper to Zinc has caused an increase in the value. It has been shown by X-ray analysis that eta is to be regarded as a solid solution of Copper in Zinc (18), (20),(21). The two marked changes in the curve at about 90% and 83% of Zinc are connected with the limits of the epilson phase. The position of the compound is not very clearly marked but will be somewhere about 85% of Zinc which is in good agreement with the generally accepted formula of $CuZn_8$. Between 70% and 80% of Zinc the curve is typical of an eutecticiferous series.

Specific Volumes.

Whilst the study of the electrolytic potential gave much useful information yet on the problem which had prompted the investigation of the Copper-Zinc alloys it confused the issue rather than clarified it. It showed that in the range of the beta constituent neither the conditions of a solid solution nor of an eutectiferous mixture prevailed. For this reason it was resolved to study the specific volume of the alloys of the Copper-Zinc series.

The determination of the specific volume of alloys is

a/

a comparatively easy physical property to measure. As a means of studying the constitution of binary alloys its utility is limited however, as it fails to differentiate between heterogeneous mixtures and solid solutions. Both types give a linear relationship between specific volume and composition. Another factor which may prove very serious is the influence of variation in grain size upon specific volume. In the study of allotropic changes where the volume change, in passing from one allotrope to another, as for example in Iron, this method of investigation finds its widest range of utility.

As all previous work on this line of attack in the Copper-Zinc series was unsatisfactory from the point of view of constitutional study, either having been done with alloys whose treatment and analyses are not recorded, or with cast alloys in the other cases, it was considered desirable to carry out a careful investigation of this property.

Previous Work.

In 1921 Bamford (22) published a paper on the Density of the Copper-Zinc Alloys. His work was carried out on chill cast and sand cast specimens. In this paper he gives a good resume of earlier work together with the graphical representation of the results of the principal workers. As Bamford showed there was little agreement between the various workers' results. The only point of significance in this work is the sharp and well-marked minimum at about 12% of copper. Bamford reported his results as relative density taking water at $4^{\circ}C$ = 1.000. He weighed his specimens in boiled distilled water.

Newbury (23) determined the density of a very few of the Copper-Zinc alloys in the course of a study of the volumes occupied by solute atoms in certain intermetallic compounds. His method was of a high order of accuracy. The specimens were weighed in distilled water and the surface tension effects of the Pt. wire were nullified by using an exactly similar/

similar wire, dipping into exactly the same depth of water, on the other arm of the balance. In his calculations he corrected for air displacement. His results are given below for sake of comparison.

| Per cent of Zn in alloy. | Density of annealed specimen. | Specific volume. |
|---|---|---|
| 4.06 | 8.884 | 0.1131 |
| 7.86 | 8.816 | 0.1134 |
| 11.66 | 8.776 | 0.1140 |
| 15.58 | 8.688 | 0.1151 |

Owen and Preston (20) in the course of an X-ray diffraction pattern study of the Cu-Zn alloys determined the densities of the alloys examined. No special precautions are reported in their paper as having been adopted to obtain very accurate results. The figures obtained by these workers are as follows.

| Per cent of Zinc in alloy. | grms./cc (annealed specimens) | Specific Volume. |
|---|---|---|
| 0 | 8.93 | 0.1120 |
| 11.35 | 8.80 | 0.1136 |
| 20.77 | 8.67 | 0.1153 |
| 27.09 | 8.57 | 0.1167 |
| 30.0 | 8.54 | 0.1171 |
| 38.73 | 8.43 | 0.1186 |
| 48.5 (quenched) | 8.32 | 0.1202 |
| 48.5 (slowly cooled) | 8.32 | 0.1202 |
| 67.2 (heated to 500 for 2 hrs & quenched in water) | 8.0 | 0.1250 |
| 80.1 | 7.77 | 0.1287 |

Still more recently Westgren and Phragmen gave a few density determinations. Here also no special precautions are reported, as having been adopted, to obtain a high order of accuracy. Their results are as follows.

| Per cent of Zinc in alloy. | Density. | Specific Volume. |
|---|---|---|
| 32.2 | 8.45 | 0.1183 |
| 46.9 | 8.32 | 0.1202 |
| 67.7 | 7.92 | 0.1263 |
| 61.7 | 8.04 | 0.1244 |
| 64.7 | 7.99 | 0.1252 |

The results tabulated in table XIV are in good agreement with the figures obtained by previous workers and, more especially so, when the difficulty of producing absolutely sound castings is taken into consideration.

Experimental work.

The method adopted was the usual Archimedian method of determining the density from which the specific volume of the alloy was calculated. From preliminary experiments it was found that the usual method of weighing the specimens in water was not sufficiently sensitive and that, by weighing in paraffin oil, much greater sensitivity was obtained. By so weighing it was comparatively easy to obtain weights in paraffin to 0.0001 grams. The density of the paraffin oil was carefully determined by means of a specific gravity bottle. The influence of temperature upon this type of experiment is very marked. The same specimen was found to vary widely from day to day due to this cause. In order to correct for this variation one specimen was taken as standard and its density carefully determined at 18°C. This specimen was then weighed before and after each determination which was made on all other specimens. The true value of the standard specimen being known and also its value under the same conditions as all other determinations it was possible to correct for temperature variations in the oil. A difference of less than 0.001 grams was obtained in the weight of the standard specimen in each determination. If it exceeded this figure it showed that the effect of the specimen on the temperature of the paraffin oil had been too great. To reduce this temperature effect of the/

the specimens on the oil to a minimum, the alloys, before weighing in paraffin, were allowed to stand in a beaker of paraffin beside the balance for a short time. Another source of serious error was found to be in the porosity of the specimens. In the early experiments it was found very difficult to obtain satisfactory duplicate results even with the use of paraffin oil as a weighing medium. Recourse was had to the method of Maey (24) of boiling the specimens in water for some time but even this device was not entirely satisfactory. Finally the specimens were subjected to a vacuum treatment under paraffin oil. For this purpose the specimens were put into a wide-mouthed suction flask into the mouth of which was fitted a rubber cork carrying a glass stop-cork. The specimen, after weighing in air, was immersed in paraffin oil in the suction flask and the flask evacuated by a Topler pump. Pumping was continued until no more bubbles rose from the specimen. After this treatment it was transferred to the beaker at the balance, being kept under paraffin all the time. Similarly it was transferred to the Platinum weighing cage. By using these precautions results could be readily duplicated. The suspension wire of the Platinum cage, used for weighing the specimens in paraffin oil, was made of very thin Platinum wire, 0.2 m.m. in diameter. As comparative results under strictly accurate and reproducable conditions were considered of first importance it was not considered necessary to correct for the very small error due to the surface tension of the wire. Care was taken to ensure the same depth of paraffin in the beaker at all determinations.

The small errors introduced by the displacement of the air by the weights and by the specimens were likewise neglected and for a similar reason, these being practically constant in each case. It may be mentioned that the weights were standardised before use and again checked before performing some farther work at a later date.

The data obtained from these determinations are given in table XI' and are set out in graphical form in Figures 7 and 8, which show respectively the density and the specific volume plotted against composition.

Discussion of Results.

The curves show in the alpha range, up to about 36.5% Zinc, a distinctly linear form. At 36.5% Zinc there is a change in direction of the curves, it being most clearly marked in the density curve, Figure 7. This change continues over the whole range of the beta constituent. From 60% to 66% Zn there is little change in density (or specific volume) but after the latter figure the curve changes very rapidly, reaching a very marked minimum in density curve, - or maximum in the specific volume curve - at 86.5% Zn. This confirms the curve of Bamford (22) which also showed a similar marked change over the same range of composition. From 86.5% Zn. to 92% Zn the curve rapidly changes once again showing a maximum at the latter composition in the case of the density curve, and a minimum on the specific volume curve. From 92% Zn up to pure Zn the curve runs smoothly.

Comparing figures 1 and 7 many points of resemblance appear in a striking manner. The limit of the alpha range is marked in both cases by a slight break in the curve. The whole range of the existence of beta in the thermal equilibrium diagram, i.e., from 36.5% Zn to 60% Zn, is marked by change in curvature in each case. From 60-66% Zinc there is an abrupt change indicated in the one case by a sudden fall and in the other by a horizontal branch. A minimum is shown in both curves at about 86.5% Zn and a maximum at about 92% Zn. The density curve does not show any clearly marked effect of the distortion results due to the Zn in copper in the alpha range or of copper in zinc in the eta range similar to that observed in the e.m.f. determinations.

Whilst/

Whilst the specific volume and density curves mark very clearly the existence of a compound at $CuZn_8$ they do not indicate whether $Cu_2Zn_3$ or $CuZn_2$ is the compound in the centre range of the series. This state of affairs is not unexpected in the light of recent X-ray analysis results. At $CuZn_6$ a very marked change in space lattice arrangement takes place, ~~eta~~ epsilon being of rhombohedral (21) type whilst gamma is of the body centred (21) variety, thus giving rise to a much more pronounced lattice change in ~~eta~~ epsilon than in gamma with a resultant greater change in density in the former case.

A brief investigation of the delta constituent was carried out. The density and specific volume of the eutectic alloy - 29.0% copper - in the quenched, annealed, and cast states were determined. From table XV it will be observed that the annealed alloy has a greater density than the quenched alloy, the cast alloy being intermediate, indicating that in the cast state the delta constituent had only partially broken down into its constituents. Figs 9, 10,11,and 12 show the photo-micrographs of these three alloys and bear out the deduction that the cast structure has not been completely resolved into gamma and epsilon.

The effect of heat treatment on the density was also investigated over the range in which the beta constituent existed, namely from 36.5% to 60% Zn. The results show a maximum effect in the beta range and also show that the intensity of quenching affects the results. It would appear that quenched beta is more dense than the annealed beta. These results are difficult to explain and more so in the light of the dilatation curves which show that there is a marked expansion in beta alloys when passing through the range of temperature 370°C. to 470°C. From the dilatation curves it would be deduced that quenched beta, assuming it to retain its high temperature state as the result of the quenching, would be less dense than the annealed state. It must be mentioned however that although the majority of the experiments yielded/

yielded results as quoted above, in one or two isolated cases a slight decrease was obtained upon quenching. How far grain growth entered into the above experiments as an upsetting factor it is impossible to say. That it is an important factor must not be overlooked in considering results of the above type. Table XVI gives the most concordant results obtained in a large series of determinations.

A series of experiments were carried out to follow any changes upon prolonged soaking of a beta brass. A piece of 53.4% Cu alloy was heated in a sealed bottle at 440°C. for varying periods of time up to a period of 6 weeks. Before each determination the surface of the specimen was removed by grinding so as to eliminate as far as practicable the effect of loss of Zinc of the outer layer. Fig. 13 shows the graphical representation of the results obtained. It should be noted that the original specimen was water-quenched from 600°C. These results appeared very satisfactory and were what was expected from a priori reasoning. However, re-quenching the specimen after its final soaking did not reproduce the original value of 8.3100 for the density but gave 8.3514 and on fracturing the specimen it was found to be very coarse. Undoubtedly alteration in grain size had played a prominent part in the change of density observed. As these experiments were running concurrently with the above experiments of heat-treatment of the beta alloys and in view of the unsatisfactory results which accrued from them this matter was not pursued further. It was considered that too many variables arose and the great redeeming feature of a change of lattice at 475°C. in Copper-Zinc alloys apparently not existing, such as is met with in iron-carbon alloys, specific volume as a line of attack upon the beta-phase change was abandoned.

Hardness.

A study of the hardness of the Cu-Zn series was thought worthy of attention as a possible source of further information upon the constitution of these alloys. For this study Shore's method was considered the more valuable, as using the standard Brinell apparatus it is invariably found that alloys in the gamma range, 30%-40% Zinc, crack under load.

Previous Work.

In most of the work already done Brinell's method has been the one adopted. Turner and Murray (25) in a paper upon the Volume changes in Copper-Zinc alloys gave results for both the Brinell and the Shore methods for a full range of alloys. In using the Shore apparatus unfortunately a hard hammer has been used and consequently very small rebounds obtained. Results for annealed and cast alloys are given but it is doubtful if the question of complete annealing received sufficient attention. In 1918 Meneghini (26) described his experiments upon the hardness of Copper-Zinc alloys. He paid especial attention to annealing and used a special type of apparatus for determining the hardness. Johnson (27) in the course of a study of the mechanical properties of Copper-Zinc alloys also determined the Brinell Hardness of these alloys. With the exception of Meneghini's data, results in the gamma range are missing.

Experimental.

Precautions as to flatness of surface and also smoothness of surface were observed and special attention was given to size of specimen. In the majority of cases more than one specimen of each composition was used and a number of determinations were made upon each specimen. In a few cases the specimens had to be mounted in the special pitch cup supplied with the apparatus, to get the necessary rigidity. The soft "magnifier hammer" was used throughout and consequently a large range of rebound was obtained for the various alloys.

The/

The data obtained is given in table XVII and is reproduced in graphical form in Figure 14. This figure is in very close agreement with that given by Meneghini (26). Table XVIII shows the figures for a beta alloy in the three different states, namely, cast, annealed and quenched.

Discussion of Results.

It is generally assumed that the alloy containing 60% Zinc, i.e. $Cu_2Zn_3$ has the maximum hardness though no figures are available for this range. In the present investigation a number of alloys in this range were available and they do not point to $Cu_2Zn_3$ as being the composition of the compound. The cusp at 65% Zn. is very significant. From theoretical considerations the position of the compound should be indicated by such a cusp. Whilst the position of the cusp cannot be considered adequate evidence to fix the composition of the compound completely, nevertheless it is very suggestive and interesting. The reappearance of a minimum point at about 85% Zn is also interesting, being in good agreement with the density curve at this point. Further than the marked effect of small quantities of Zinc dissolved in Copper and of Copper in Zinc upon the hardness curve, nothing of importance is revealed. The effect, just referred to, is undoubtedly caused by the straining of the respective lattices by the stronger atoms as discussed under electrolytic potential measurements.

In the heat treated beta alloy it is worthy of note that the quenched state is much harder than the annealed state. This may be connected with the critical size of the separating particles from the solid solution phase rather than the retention of the high temperature state. Edwards and Herbert (28) have shown the high temperature phase is softer than the low temperature phase. They found a sudden and remarkable fall in the hardness of beta alloys on passing through the 475°C. change point. It is very remarkable that the quenched

specimen/

specimen should have a greater density and yet be harder than in the annealed state.

While the results derived from a study of electrolytic potential measurements, density and hardness determinations, have yielded very interesting results they have failed to throw much light upon the nature of the change at 470°C. in the beta brasses. That this change is one involving considerable energy change can be seen from Figure 15 which shows the thermal cooling curve for an alloy containing 53.4% of copper. Attention was now focussed entirely upon this problem and the subject was attacked from a number of different standpoints.

Dilatation.

The first method employed was to measure the coefficients of expansion of the alpha, beta, and gamma phases with increasing temperature. The dilatometer used was of the type designed by Andrew and his colleagues (29). The heating furnace was a platinum-wound silica tube, 18 inches long and 1¼ inches internal diameter. The specimens used were ¾ inch in diameter and 2 inches long, having machined ends. Ground silica discs were placed against each end of the specimen. These discs were pressed against the ends of specimen by thick-walled silica tubes which served to transmit any linear change in the specimen under test. One silica tube butted against the wall of the room whilst the other pressed against the steel diaphragm of the dilatation measuring apparatus. The movement of the steel diaphragm displaced water from the water reservoir. So that only movement of water would take place the reservoir was firmly anchored in a heavy lead block weighing about 2 cwts. The water displaced from the steel reservoir passed along a glass tube of fine bore, to which was fixed a graduated scale. By this means any change in volume in the specimen due to heating was considerably magnified. If necessary, the instrument can be calibrated by determining the dilatation of a copper specimen since the coefficient/

coefficient of expansion of copper is accurately known. In the present case that was not necessary. The temperature of the specimen was measured by means of a Platinum Platinum-Iridium couple, this being standardised before use. The temperature in the majority of cases was measured as the e.m.f. of the couple, this being obtained by means of a Tinsley Vernier Potentiometer. By taking dilatation measurements on the scale for equal increments of temperature the rate of change of dilatation with temperature can be obtained.

Five alloys were carefully analysed by this method. These were so chosen as to give the dilatation curves for the 3 phases in the following manner: alpha, alpha and beta, beta, beta and gamma, and gamma. The curves are shown in figures 16 to 20 inclusive.

The most striking feature of the curves is that whilst the curves for the alpha and gamma alloys are linear, that for the beta constituent shows a considerable divergence from a simple linear function throughout its course. The change of direction over the transformation range was not aharp and sudden as is the case in steels but was gradual, though nevertheless clearly marked. The change took place over a considerable range of temperature. It began at 330°C. and continued up to a temperature of 475°C. That it is not merely a change due to the specimen softening is clearly shown in Figure 18. Here it is shown that the cooling curve retraces practically the steps of the heating curve. Furthermore this change is one which does not complete itself at any temperature below 470°C, even after prolonged soaking. See fig. 18. In curve (c) the specimen was soaked for 3 hours at 460°C. On heating it showed the same increased rate of expansion up to 475°C. and then gave the coefficient of expansion of the solid solution. In curve (b) the time taken to pass over range from 330°C. to 475°C. was 5 hours which is a very slow rate of heating and yet the curve is similar to that of (a) in which the time of heating from start to finish occupied

only/

only 1 hour 10 minutes.

In Figure 21 the ordinates are obtained by taking the amount of the change of expansion in the specimens over the range of temperature from 330°C. to 475°C., i.e., they represent the rate of change of the coefficient of expansion over this range. As is seen by inspection of the curves the rate of change of expansion is zero at all points except within this range of temperature in the specimens which contain the beta constituent. Moreover as Figure 21 clearly demonstrates, the rate of change is greatest when the amount of beta is greatest and consequently must be intimately connected with it.

A beta alloy containing 53.4% of copper in suitable form was quenched in water from 600°C. and the dilatation curve determined. From the quenched state the type of curve obtained is very different from the annealed curve. Such a curve is shown in Figure 22. It will be observed that the curve rises in linear form very rapidly up to 300 m.v. (270°C). From this temperature to 330°C. the curve follows the completely annealed form and at 330°C. shows a gradual increase in rate of expansion up to a temperature in neighbourhood of 500°C. Excepting that the upper point is somewhat raised, the curve follows very closely that of an annealed specimen from 300 millivolts (270°C). The direction which the annealed curve follows below this temperature is shown by a dotted line. It is to be observed that the actual dilatation curve is much below this line at ordinary temperatures. This curve bears out the results obtained in the density determinations of quenched beta alloys, the quenched alloys having been found to have a higher density than the annealed specimens. It is to be expected that the degree of thoroughness of the quench will determine the results obtained.

The result of the investigation of the variation of the coefficient of expansion with temperature was surprising and was not in good agreement with either Carpenter and Edward's (1) view/

view of the change which necessitated a uniform expansion to the neighbourhood of 475°C. or with Hudson's (3) idea of a polymorphic transformation. The gradual change extending over a range of 140°C. and not completing itself on prolonged soaking within the transformation range, seemed very perplexing.

It was deemed desirable to do a little work somewhat along the lines of Hudson.[3] For this purpose a rod of pure copper was inserted into molten zinc and maintained in the zinc bath at a temperature of 500°C. for varying periods of time. After the first day a piece of Copper rod was cut off and the rod replaced. Altogether the experiment was carried out for a period of 4 days, a piece being cut off the rod at intervals, heating continuously throughout the 24 hours. Photo-micrographs of the two typical sections are shown in Figures 23 and 24. These merely show a ring of white brittle gamma which changes a little in colour, then a marked change to a yellow band of beta, followed by another sharp change to alpha which gradually passes to Copper.

A similar experiment was carried out at 400°C. which gave precisely similar results. Figures 25-26 show the appearance of the various sections when examined microscopically. This bears out the work of Hudson.

As pure Copper and pure Zinc under diffusion gave no definite clue to the phases involved in the 470°C. change point, the yellow band in both experiments appearing exactly alike, an endeavour was made to obtain some microscopic difference in another way. For this purpose an alloy containing 35% Zn had a hole drilled into it to a depth of about one inch. Into this hole was rammed powdered gamma constituent containing 61% Zn. This specimen was carefully heated to 440°C. and maintained at this temperature for a number of hours. On examination the results were the same as before - a yellow band of beta had been formed round the edge of the hole in the 35% Zn alloy. see Fig. 27

It/

It is of interest to note that Masing (30) has carried out similar work and obtained the same results. He heated together at 400°C. for 20 hours chips (spāne) of alpha and gamma and on micro-examination obtained a golden yellow constituent between the remaining alpha and gamma particles. This he identified as beta. He showed that on heating the same compounds at 200°C. for a very long time - 118 hours - a very thin film of the yellow beta was formed.

Attention was now turned to Carpenter's (31) work on the influence of special elements upon the beta change at 475°C. In his classical paper in 1912 the most remarkable result is undoubtedly the effect of 2.9% Bismuth upon the change. This addition caused a complete breakdown of the beta into alpha and gamma constituents while lesser or greater quantities of Bismuth either were not so effective, or gave practically no result.

The following experiments were carried out. To a beta brass containing 52% of Copper were added small quantities of Bismuth, Vanadium, Antimony and Tin. The alloys were annealed and very slowly cooled in the furnace. They were then microscopically examined. The results are set out in tabular form below.

| Amount of Added Element. | Microscopic Appearance. |
|---|---|
| 0.5 per cent of Bismuth. | Uniform beta; this small quantity had no effect upon the stability of the beta phase which confirms Carpenter's observation. |
| 0.5 per cent of Antimony. | Uniform beta. |
| 0.5 per cent of Vanadium. | A very fine duplex structure. Carpenter found that Vanadium was very active in bringing about the resolution of the beta into alpha and gamma. Structure is shown in Figure 28. |
| 0.5 per cent of Tin. | A very fine duplex structure similar to previous example. |
| 1.0 per cent of Tin. | Eutectoid structure is very clearly developed as shown in Figure 29. |
| 2.0 per cent of Tin. | Eutectoid structure is still more fully resolved. |

Even more striking is the result obtained by Heike and Ledebur (32). These workers obtained complete resolution of beta into alpha + gamma by the addition of 15% of Manganese to a beta alloy. They also showed that by adding 15% of Manganese to an alloy containing 45% Copper that the gamma primary crystals were obtained in a groundmass of eutectoid, and similarly by adding 15% Manganese to an alloy containing 63% Copper, large primary alpha crystals were got in an eutectoid background. These experiments further supplement Carpenter's (31) evidence that it is actually the beta constituent that is broken down. Moreover their work brings out this point, that the amount of the added constituent is of vital importance. Carpenter (31) tried the effect of Manganese in his experiments but did not use more than 5% of Manganese in his alloys. He found that Manganese had no effect on the stability of the alloy. Had he tried 15% he would have got the same thing as he found with Bismuth.

In Masing's work (30) record is made of an experiment along similar lines but as he used 5% of Aluminium and 3% of Tin it is not very convincing but is useful corroboration of the previous examples. He took a Copper alloy containing 3% of Tin and 5% of Aluminium, and drilled a hole in it. Into this he put Zinc and heated the specimen for 5 hours at 450°C. He obtained a broad band of gamma between the dark Zinc and the gray Copper alloy. Repeating the experiment using pure Copper in place of the alloy he got a broad band of gamma as before but between the gamma and the copper (it would really be alpha at the zinc side) there was a distinct narrow yellow band of beta.

The results of the experiments upon diffusion at various temperatures and of the influence of added elements apparently leads to what at first sight appears a paradox. It would appear from the diffusion experiments that the polymorphic version is correct and that alpha and gamma do not exist together as the stable/

stable phases at low temperatures whereas the experiments with added elements show that provided the correct substances are added, and added in the right amount, the beta constituent can be resolved into alpha and gamma. The latter statement clearly points to the view that the added element, say Manganese, allows of the separation of the particles by possibly reducing the surface tension. It seems most probable that below 470°C. the constituents are present in a very finely divided state, of dimensions under microscopic size, and that, in fact, we have a colloidal solution. Mere soaking alone will not cause these particles to coalesce, due, very possibly, to the electronic configuration of the particles, or may be to the fact that the particles carry a change though this is not necessarily the case. M'Bain's (33) work in soap solutions gives definite evidence of the fact that we can have electrically neutral colloidal particles. The effect of the added element is to alter the electronic configuration so as to allow of coalescence - in other words, to alter the surface forces or surface tension. Giolètte has recently suggested that the action of Manganese in steel is of the same order, that is, it alters the surface tension at the non-metallic/steel interface and so allows of impurities rising more readily to the surface in the ingot mould.

The vapour tension of Zinc has been calculated by Richards (35) who found that even at 248°C. Zinc has a vapour tension of 0.0002 m.m. of Mercury in vacuo. Thus, even at very low temperatures Zinc has quite an appreciable vapour tension. The values for the vapour tension of Zinc for the various Copper Zinc alloys have not been computed in terms of millimetres of Mercury but from the work of Turner and Thorneycroft (36) it can readily be seen that in the Zinc rich alloys the vapour tension must be considerable. Their figures show that the loss of Zinc in the gamma alloy is considerable at 460°C. whilst at the same temperature the loss of Zinc in the alpha constituent

is/

is negligible. Thus where gamma or Zinc is used in diffusion experiments the vapour tension of the Zinc may be a very momentous factor in bringing about the result produced.

That diffusion takes place through the medium of the vapour phase has been shown by Andrew and Higgins (37). If the case of two substances A and B be considered in a general way, A will diffuse into B and B into A but not necessarily at the same rates. Each will advance at a characteristic rate of its own, which will be a function of the vapour tension. Desch in his presidential address to the Chemistry section of the British Association, 1925, stated that it had been shown in his laboratories that Copper diffuses into Nickel 20 times faster than Nickel into Copper. Similarly from a study of the vapour tensions it should be expected that Zinc will diffuse into Copper at a very much faster rate than Copper will diffuse into Zinc. In the case of the experiment of the Copper rod in Zinc the centre portion of the Copper rod still had the appearance of Copper and only gradually changed to a brass colour. The changes observed are shown diagrammatically in Figure 30.

From the edge of the Copper zone the concentration of Zinc gradually rose until saturated alpha was reached. Then the golden yellow, clearly defined beta zone made its appearance. The Zinc atoms, that is Zinc vapour, as opposed to solid Zinc with its lattice, must necessarily have advanced over this zone so that the concentration in Zinc gradually rose until the gamma made its appearance. Similarly over the white brittle gamma zone a variation in concentration must have existed from free Zinc at one side, through the compound with Zinc in solution. The widths of the bands (or amounts of the phases) formed will naturally be controlled by the variation of the vapour tension of the different phases. Moreover temperature will play an important part in the amount of the various phases found as the vapour tension of the Zinc, and to a much lesser extent of the Copper, will vary appreciably with temperature. This

is well shown in Figures 28 and 29.

It is now easy to understand why Hudson failed to obtain alpha + gamma when soaking either Copper or 70/30 Brass in Zinc at 450°C. and why similar experiments in the present work also produced only the yellow beta. It is more difficult to explain why Carpenter succeeded in resolving beta at a temperature of 450°C. and why Hudson should have failed when repeating the experiment. Assuming that both experimenters used pure materials the only available explanation is some difference in pressure as the temperatures were the same both cases. No details are given upon this point. If, in one case, the tube was not evacuated then there would be an increase in pressure of $2\frac{1}{3}$ times the initial state. How far this might affect the results it is difficult to say. It is worthy of mention that Carpenter and Edwards in their original paper state that the specimens were heated to a temperature of 350°C., a temperature at which the vapour tension of Zinc in the alloy will be very small. The physical properties which have been experimentally investigated point, very decidedly, to the fact that the 470°C. change in the beta phase is a gradual one. Further evidence on this point is found in Figure 31 in which the figures obtained by Doerinckel and Werner (38) for the Specific Heats of alloys of varying composition are plotted. In both the cast and annealed states there is a marked change in the direction of the curve between 400° and 500°C. Moreover the curve commences to rise at 330°C. and then rises more rapidly as the temperature of 470°C. is approached, the change in the case of the "tempered" alloy completing itself at about this temperature. It is also to be noted that, as the change approaches completion, more and more energy is required to bring it about.

The work of Hiroshi Imai (4) adds further proof of the gradual nature of this change. From a study of resistivity-temperature measurements Imai found that the rate of change of resistivity increased as the amount of beta increased.

His/

His explanation of the phenomenon is that it is neither of the eutectoid type nor of the polymorphic transformation order but is similar to the $A_2$ change in iron. He found that on soaking in the transformation range for 80 minutes it made no change on the resistivity; that is, the change did not complete itself, a point which has already been referred to in the dilatation studies of the beta brasses. Imai assumes a change in the gamma phase, similar to that in the beta range, from his resistivity curves although his thermal work is unfavourable to this view. To get over this difficulty he assumes that the thermal effect accompanying the transformation of gamma is very small compared with that of the beta transformation.

That this change in beta is due to a magnetic change is not well supported by the dilatation curves. In pure Armco Iron in which the $A_2$ change is very much more pronounced there is, at most, only a very slight change in direction due to the $A_2$ transformation; that it is very much smaller than that of the beta alloy is shown in Figure 32.

All evidence would appear to rule out such explanations as a simple eutectoid change, a polymorphic transformation and a magnetic transformation. There still remains the possibility, already referred to, of the change being of an eutectoid nature but the separating phases of the eutectoid being in the colloidal state. This idea was first suggested by Professor Andrew as a result of the study of the dilatation curves and this view has already been shown to be supported by the work of Carpenter and Masing on the effect of additional elements on the beta constituent. If this suggestion be correct, then it is highly probable that the electronic configuration could be upset by submitting a specimen to the influence of a current of suitable voltage. Experiments were conducted along these lines and the results of treating an alloy containing 53% Copper with alternating current at 400°C. is shown in Figure 33. This structure was reproduced, in all, ten times on different specimens of the same composition.

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In these experiments the method adopted was to heat a thin rod of about ¼ inch diameter in an electric furnace to 400°C. The furnace was maintained at this temperature for a few hours. The specimen was connected to the secondary circuit of an induction coil giving about 50,000 volts and was subjected to the influence of this current while it was in the furnace. The specimen, after treatment, was cut in two pieces and one piece polished for micro-examination. The cut face was always polished. In order to obtain a well-defined structure it was found very helpful to rub the specimen lightly on the hand after etching. The etching reagent used was a mixture of ammonia, ammonium persulphate and hydrogen peroxide. No doubt the reason why the gamma did not appear so evident after etching alone, was due to the fact that a thin film of Copper was deposited on the gamma particles. It was repeatedly observed during the electrolytic potential determinations of the gamma alloys that Copper was deposited very rapidly on their surface when immersed in copper electrolytes. Therefore it is to be expected that the copper which immediately goes into solution from the alpha phase of the alloy on etching would be precipitated in small amount on the gamma constituent.

The duplex structure was obtained on one occasion by treating the specimen with direct current but it was not well resolved. Prolonged soaking at 440°C. without treatment did not produce this duplex structure.

A new beta alloy was made and on analysing at the end of the treatment was found to contain 53.8% of copper. On this occasion the bar was half an inch in diameter and 2½ inches long. A lower temperature of soaking was adopted in this case, namely 330°C. Soaking alone at this temperature produced a very fine duplex structure but by treating the specimen at 330°C. with alternating current for 12 hours a very much better resolved structure was obtained. Figure 34 shows the appearance of the specimen after etching. This specimen was next heated at 700°C., maintained/

maintained at this temperature for 20 minutes and then slowly cooled in the furnace. Figure 35 shows the structure obtained after cutting, polishing, and etching the specimen. It is noted that the structure is that of the usual beta brass, showing large apparently uniform grains. Figure 36 shows the microstructure of a piece of the same specimen after treatment with alternating current at a temperature of 330°C. for 2 days continuously. In this case the specimen was not rubbed on the hand as the gamma constituent, being very massive, was easily distinguished.

Another alloy was cast and this time it contained 52.1% of copper. Like the previous alloys it was annealed until all cast structure was obliterated and then treated as already described at a temperature of 300°C. In this case the duplex structure was visible under high magnifications but the constituents were not as well resolved as in the earlier specimens.

It has been shown that the beta constituent of the Copper-Zinc series is of a colloidal nature and this explanation is in full accord with the experimental data. It has been shown that quenching increased the hardness of these alloys. This is due to the presence of the finely dispersed particles whereas in the slowly cooled alloy, although the particles are still submicroscopic, they must be very much larger than in the quenched state. This is exactly parallel to the phenomena in steel. It is now generally accepted that alpha iron is the basis of martensite. Martensite is very much harder than the solid solution Austenite, and it is now being advanced by Bain (39) and others that Martensite is a colloidal solution of very finely dispersed carbide of iron in alpha iron. The colloidal view is also borne out by the following experiment. A quenched 0.71% carbon steel was subjected to alternating current treatment at room temperature in the same manner as described later under Duralumin, and its Brinell hardness was reduced from 650 in the quenched state to 550 after treatment. Troostite is generally regarded as being of/

of a colloidal nature because the carbide of iron is sub-microscopic, yet it is much softer than Martensite. The fundamental difference between the two constituents lies in the degree of dispersion of the separating phase and is thus parallel to the case of the beta brasses.

The reason for the gradual change in the direction of the dilatation curves of the beta alloys now becomes evident. The very finely divided particles of the separating phase will go into solution at a lower temperature than the more massive material so that, from about 330°C. to the change point at 475°C., the separated material will go gradually into solution and so cause a change in the coefficient of expansion. This will also account for the gradual increase in resistivity over the same temperature range which was observed by Iamai (4).

The thermal analysis of the beta brasses by Roberts Austen (2) and by Matsuda (40) add further weight to this view of the 470°C. change point. In Figure 3 are plotted the results obtained from their work. It will be noted that the change point is gradually depressed from 475°C. to 450°C. as the copper content of the alloys is increased. The significance of the gradual depression of the point of maximum thermal effect is that the transformation has been lowered and this is brought about with increasing copper content. It would seem highly probable that 475°C. represents the true equilibrium change point but that, as the amount of the gamma constituent becomes less, it (the gamma) will be present in a more disperse state and so further lower the change point. That the degree of dispersion has a marked influence upon the phase change point has been shown by various workers. P.Pawlow (41) found for finely powdered Salol, and Antipyrin that, with very small individual particles, the melting point was 7°C. below that obtained when using larger particles.

From the foregoing study of the Copper-Zinc system the most important points which have emerged are:-

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1. The addition of Zinc up to 10% to Copper causes a very marked strain in the lattice but further additions do not produce any appreciable increase in the strain.
2. The transformation in the beta constituent at 470°C. is of an eutectoidal nature but the separating phase is in the colloidal state.
3. Quenching of beta alloys produces increased hardness, which increases with the severity of the quenching.
4. Evidence was produced to show that $Cu_2Zn_3$ is not the formula of the intermetallic compound of the gamma range. It was shown to lie at about 33% of Copper whence $CuZn_2$ more nearly approaches to the formula of the compound.
5. The density of the delta constituent is less than the density of the eutectoid mixture of gamma and epsilon.
6. A sharp minimum was observed on the density-composition curve at 13.5% of copper thus confirming the work of Bamford (22). This point marks the position of the compound $CuZn_8$ whose space lattice pattern is of the hexagonal form and so differs widely from that of the gamma compound which has a lattice of the cube centred type.
7. The addition of Copper to Zinc produces the same result as adding Zinc to Copper, namely it causes a strain in the lattice of the Zinc.

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Table I.

| % Cu. | % Zn. | Deflection of Galvanometer. | Tan. of half angle of Deflection. | E.M.F. in volts. |
|---|---|---|---|---|
| 100.00 | 0 | 43 | 0.0188 | 0.153 |
| 91.92 | 8.08 | 34 | 0.0156 | 0.130 |
| 85.75 | 14.25 | 40 | 0.0184 | 0.150 |
| 72.99 | 87.07 | 43 | 0.0188 | 0.153 |
| 66.70 | 33.30 | 47 | 0.0126 | 0.176 |
| 49.32 | 40.68 | 55 | 0.0253 | 0.206 |
| 27.99 | 72.07 | 115 | 0.0529 | 0.432 |
| 7.53 | 92.47 | 203 | 0.0939 | 0.768 |
| 0.0 | 100.00 | 234 | 0.1763 | 1.442 |

Table II.

| % Cu. | % Zn. | E.M.F. in volts. |
|---|---|---|
| 100 | 0 | -0.200 |
| 75 | 25 | -0.200 |
| 54.4 | 45.6 | +0.040 |
| 50.5 | 49.5 | 0.070 |
| 49.3 | 50.7 | 0.070 |
| 47.2 | 52.8 | 0.075 |
| 46.1 | 53.9 | 0.065 |
| 43.9 | 56.1 | 0.070 |
| 41.7 | 58.3 | 0.080 |
| 37.0 | 63.0 | 0.085 |
| 36.5 | 63.5 | 0.085 |
| 35.9 | 64.1 | 0.160 |
| 33.8 | 66.2 | 0.530 |
| 30.3 | 69.7 | 0.570 |
| 29.2 | 70.8 | 0.600 |
| 28.0 | 72.0 | 0.580 |

Table III.

| Atomic percentage of Copper in Alloy. | Atomic percentage of Zn. in Alloy. | Potential Difference in millivolts. | (calculated by author) Electro-motive force between Alloy and $\frac{N}{1}$ $Zn.SO_4$ assuming $Zn/\frac{N}{1}$ $Zn.SO_4$ to be .520 volts. |
|---|---|---|---|
| 10.3 | 89.7 | 5.4 | .5146 |
| 16.4 | 83.6 | 5.2 | .5148 |
| 23.5 | 76.5 | 5.3 | .5147 |
| 30.99 | 69.01 | 5.7 | .5143 |
| 33.97 | 66.03 | 728.0 | .208 |
| 39.7 | 60.3 | 728.0 | .208 |
| 45.7 | 54.3 | 784.0 | .264 |
| 50.8 | 49.2 | 932.0 | .412 |
| 60.7 | 39.3 | 1000.0 | .480 |
| 76.3 | 23.7 | 1020.0 | .500 |
| 100.0 | 0. | 1130.0? | .610 |

Table IV.

| Atomic percentage of Copper in Alloy. | Potential difference in millivolts. | (calculated by author) Electro-motive force between Alloy and $Zn.SO_4$ assuming $Zn/\frac{N}{1}$ $Zn.SO_4$ to be .520 volts. |
|---|---|---|
| 100 | 1010 | .490 |
| 90 | 960 | .440 |
| 85 | 960 | .440 |
| 80 | 960 | .440 |
| 75 | .985 | .465 |
| 70 | 1000 | .480 |
| 68 | 960 | .440 |
| 65 | 918 | .398 |
| 62 | 920 | .400 |
| 57 | 918 | .398 |
| 55 | 921 | .401 |
| 53 | 835 | .315 |
| 50 | 800 . | .280 |
| 47 | 800 | .280 |
| 43 | 800 | .280 |
| 40 | 800 | .280 |
| 37 | 730 | .210 |
| 36 | 722 | .202 |
| 35 | 545 | .025 |
| 32 | 39 | .481 |
| 30 | 24 | .496 |
| 23 | 28 | .492 |
| 20.6 | 30 | .490 |
| 20 | 38 | .482 |
| 19 | 28 | .492 |
| 18 | 37 | .483 |
| 17 | 33 | .487 |
| 16 | 40 | .480 |
| 15 | 26 | .494 |
| 13 | -3 | .523 |
| 12 | -7 | .527 |
| 11 | -3 | .523 |
| 10 | -3 | .523 |
| 5 | -3 | .523 |

## Table V.

| Molar Concentration. | $\frac{1}{2}$ $Zn.SO_4$. | $\frac{1}{2}$ $Cu.SO_4$. | Calculated on assumption that complete dissociation at .0001 Mol. Conc. for $Zn.SO_4$. | for $Cu.SO_4$. |
|---|---|---|---|---|
| .0001 | 109.3 | 113.3 | 1.0 | 1.0 |
| .0002 | 107.2 | 111.1 | 0.98 | 0.98 |
| .0005 | 103.1 | 106.8 | 0.945 | 0.941 |
| .001 | 98.4 | 101.6 | 0.90 | 0.897 |
| .002 | 92.2 | 93.4 | 0.844 | 0.825 |
| .005 | 82.0 | 81.5 | 0.75 | 0.719 |
| .01 | 73.4 | 72.2 | 0.671 | 0.635 |
| .02 | 64.8 | 63.0 | 0.593 | 0.555 |
| .03 | 59.5 | 57.4 | 0.545 | 0.505 |
| .05 | 53.3 | 51.4 | 0.489 | 0.454 |
| .1 | 46.2 | 45.0 | 0.421 | 0.398 |
| .2 | 40.1 | 39.2 | 0.366 | 0.346 |
| .3 | 36.8 | 35.5 | 0.337 | 0.313 |
| .5 | 32.3 | 30.8 | 0.296 | 0.272 |
| 1.0 | 28.6 | 25.8 | 0.242 | 0.2275 |

## Table VI.

### 1st Series of Alloys.

| Cast Mark. | Composition. | | Atomic Percentage of Copper. |
|---|---|---|---|
| | Percentage of Copper. | Percentage of Zinc. | |
| A. | 89.7 | 10.3 | 90.0 |
| B. | 81.4 | 18.6 | 82.0 |
| C. | 69.6 | 30.4 | 69.9 |
| D. | 60.1 | 39.9 | 60.0 |
| E. | 49.1 | 50.9 | 49.5 |
| F. | 45.0 | 55.0 | 45.4 |
| G. | 43.3 | 56.7 | 43.8 |
| H. | 40.5 | 59.5 | 41.0 |
| I. | 39.5 | 60.5 | 40.0 |
| J. | 27.8 | 72.2 | 28.3 |
| K. | 25.2 | 74.8 | 25.6 |

Table VII.

$Hg/Hg_2Cl_2$ in KCl $\frac{N}{1}$/$\frac{N}{1}$ KCl/$\frac{N}{1}$ $Cu.SO_4$/ Alloy.

| No. of Alloy. | Sign of Calomel Cell. | Potentiometer Reading in volts. | Electro-motive Force between alloy and $\frac{N}{1}$ $Cu.SO_4$ solution. |
|---|---|---|---|
| A. | negative. | .029 | .589 |
| B. | negative. | .028 | .588 |
| C. | negative. | .026 | .586 |
| D. | negative. | .012 | .572 |
| E. | negative. | .010 | .570 |
| F. | negative. | .006 | .566 |
| G. | negative. | .007 | .567 |
| H. | positive. | .024 | .536 |
| I. | positive. | .040 | .520 |

Table VIII.

$Hg/Hg_2Cl_2$ in $\frac{N}{1}$ KCl/$\frac{N}{1}$ KCl/$\frac{N}{1}$ $Zn.SO_4$/ Alloy.

| No. of alloy. | Sign of Calomel Cell. | Potentiometer Reading in Volts. | Electro-motive Force between alloy and $\frac{N}{1}$ $Zn.SO_4$ solution. |
|---|---|---|---|
| A. | positive. | .063 | .497 |
| B. | positive. | .060 | .500 |
| C. | positive. | .063 | .497 |
| D. | positive. | .087 | .473 |
| E. | positive. | .205 | .355 |
| I. | positive | .310 | .250 |
| J. | positive. | .778 | .218 |
| K. | positive. | .845 | .285 |
| Zn. | positive. | 1.0635 | .5035 |
| Cu. | positive. | .07 | .490 |

Table IX.

Second Series of Alloys.

| Cast Mark. | Composition. Percentage of Copper. | Composition. Percentage of Zinc. | Atomic Percentage of Copper. |
|---|---|---|---|
| 1. | 95.0 | 5.0 | 95.15 |
| 2. | 90.0 | 10.0 | 90.25 |
| 3. | 85.0 | 15.0 | 85.3 |
| 4. | 80.0 | 20.0 | 80.4 |
| 5. | 76.0 | 24.0 | 76.5 |
| 6. | 67.4 | 32.6 | 68.0 |
| 7. | 56.0 | 44.0 | 56.4 |
| 8. | 53.0 | 47.0 | 53.4 |
| 9. | 48.8 | 51.2 | 49.2 |
| 10. | 45.9 | 54.1 | 46.3 |
| 11. | 40.2 | 59.8 | 40.6 |
| 12. | 37.0 | 63.0 | 37.5 |
| 13. | 35.0 | 65.0 | 35.4 |
| 14. | 34.0 | 66.0 | 34.5 |
| 15. | 32.0 | 68.0 | 32.4 |
| 16. | 27.8 | 72.2 | 28.2 |
| 17. | 18.3 | 81.7 | 18.7 |
| 18. | 18.0 | 82.0 | 18.4 |
| 19. | 16.9 | 83.1 | 17.3 |
| 20. | 15.6 | 84.4 | 16.0 |
| 21. | 13.58 | 86.42 | 13.9 |
| 22. | 13.5 | 86.5 | 13.8 |
| 23. | 8.3 | 91.7 | 8.7 |
| 24. | 2.8 | 97.2 | 3.1 |
| 25. | 2.0 | 98.0 | 2.2 |

## Table X.

$Hg/Hg_2Cl_2$ in KCl $\frac{N}{1}/\frac{N}{1}$ KCl/$\frac{N}{1}$ $Cu.SO_4$/Alloy.

| No. of Alloy. | Sign of Calomel Cell. | Potentiometer Reading in Volts. | Electro-motive Force between alloy and $\frac{N}{1}$ $Cu.SO_4$ solution. |
|---|---|---|---|
| Copper. | negative. | .025 | .585 |
| 1. | negative. | .030 | .590 |
| 2. | negative. | .033 | .593 |
| 3. | negative. | .030 | .590 |
| 4. | negative. | .028 | .588 |
| 5. | negative. | .027 | .587 |
| 6. | negative. | .025 | .585 |
| 7. | negative. | .017 | .577 |
| 8. | negative. | .0125 | .5725 |
| 9. | negative. | .00 | .560 |
| 10. | positive. | .004 | .556 |
| 11. | positive. | .023 | .537 |
| 16. | positive. | .64 | .080 |
| 17. | positive. | .758 | .198 |
| 19. | positive. | .81 | .250 |
| 22. | positive. | .82 | .260 |
| 24. | positive. | .94 | .380 |
| 25. | positive. | .93 | .370 |
| Zinc. | positive. | .92 | .360 |

## Table XI.

Hg/Hg Cl in $\frac{N}{1}$ KCl/$\frac{N}{1}$ KCl/$\frac{N}{1}$ $Zn.SO_4$/ Alloy.

| No. of Alloy. | Sign of Calomel Cell. | Potentiometer Reading in Volts. | Electro-motive Force between alloy and $\frac{N}{1}$ $Zn.SO_4$ solution. |
|---|---|---|---|
| Copper. | positive. | .068 | .490 |
| 2. | positive. | .071 | .489 |
| 3. | positive. | .052 | .508 |
| 4. | positive. | .052 | .508 |
| 5. | positive. | .060 | .500 |
| 6. | positive. | .058 | .502 |
| 7. | positive. | .061 | .499 |
| 8. | positive. | .089 | .471 |
| 9. | positive. | .160 | .400 |
| 10. | positive. | .192 | .368 |
| 11. | positive. | .350 | .210? |
| 12. | positive. | .295 | .265 |
| 13. | positive. | .390 | .170 |
| 14. | positive. | .670 | .110 |
| 15. | positive. | .850 | .290 |
| 16. | positive. | .852 | .292 |
| 17. | positive. | .925 | .365 |
| 18. | positive. | .953 | .393 |
| 19. | positive. | 1.015 | .455 |
| 20. | positive. | 1.026 | .466 |
| 21. | positive. | 1.020 | .460 |
| 22. | positive. | 1.013 | .453 |
| 23. | positive. | 1.076 | .516 |
| 24. | positive. | 1.074 | .514 |
| 25. | positive. | 1.068 | .508 |
| Zn. | positive. | 1.064 | .504 |

Table XII.

$Hg/Hg_2Cl_2$ in $\frac{N}{1}$ KCl/$\frac{N}{1}$ KCl/$\frac{N}{1}$ $Zn.SO_4$ + $\frac{N}{1}$ $Cu.SO_4$ / alloy.

| No. of alloy. | Sign of Calomel Cell. | Potentiometer Reading in Volts. | Electro-motive Force between alloy and mixed electrolyte. |
|---|---|---|---|
| Copper. | negative. | .025 | .585 |
| 2. | negative. | .033 | .593 |
| 3. | negative. | .030 | .590 |
| 4. | negative. | .027 | .587 |
| 5. | negative. | .025 | .585 |
| 6. | negative. | .019 | .579 |
| D. | negative. | .0065 | .5665 |
| 8. | negative. | .0085 | .5685 |
| 9. | positive. | .004 | .556 |
| 10. | positive. | .015 | .545 |
| 16. | positive. | .685 | .125 |
| 19. | positive. | .860 | .300 |
| 21. | positive. | .874 | .314 |
| 24. | positive. | 1.039 | .479 |
| 25. | positive. | 1.037 | .477 |
| Zinc. | positive. | 1.062 | .502 |

## Table XIII.

Cell:- $Hg/Hg_2Cl_2$ in $\frac{N}{1}$ KCl/$\frac{N}{1}$ KCl/$\frac{N}{1}$ $Cu.SO_4$/ Alloy.

| No. of alloy. | Composition of Alloy. | | Potentiometer Reading in Volts. | | Electro-motive Force between alloy and $\frac{N}{1}$ $Cu.SO_4$. | |
|---|---|---|---|---|---|---|
| | %age of Copper. | %age of Zinc. | Quenched. | Annealed. | Quenched. | Annealed. |
| 3. | 85.0 | 15.0 | .030 | .030 | .590 | .590 |
| 4. | 80.0 | 20.0 | .028 | .038 | .588 | .588 |
| 6. | 67.4 | 32.6 | .024 | .025 | .584 | .585 |
| 8. | 53.0 | 47.0 | .018 | .014 | .578 | .574 |
| 8a. | 53.4 | 46.6 | .0165 | .0125 | .5765 | .5725 |
| 9. | 48.8 | 51.2 | .008 | .000 | .568 | .560 |

Cell:- $Hg/Hg_2Cl_2$ in $\frac{N}{1}$ KCl/$\frac{N}{1}$ KCl/$\frac{N}{1}$ $Cu.SO_4$ and $\frac{N}{1}$ $Zn.SO_4$ / Alloy.

| Composition of Alloy. | | Potentiometer Reading in Volts. | | Electro-motive Force between alloy and mixed solution. | |
|---|---|---|---|---|---|
| % Cu. | % Zn. | Quenched. | Annealed. | Quenched. | Annealed. |
| 53.0 | 47.0 | .0085 | .0025 | .5685 | .5625 |

Table XIV.

| Cast Mark. | Per cent Copper by weight. | Per cent Zinc by weight. | Density. | Specific Volume. |
|---|---|---|---|---|
| 2. | 90.0 | 10.0 | 8.7700 | 0.1140 |
| 3. | 85.0 | 15.0 | 8.6935 | 0.1151 |
| 4. | 80.0 | 20.0 | 8.6569 | 0.1158 |
| 5. | 76.0 | 24.0 | 8.5593 | 0.1169 |
| 6. | 67.4 | 32.6 | 8.4434 | 0.1185 |
| D. | 60.1 | 39.9 | 8.3720 | 0.1195 |
| 7. | 56.0 | 44.0 | 8.3282 | 0.1201 |
| 8. | 53.4 | 46.6 | 8.2992 | 0.1205 |
| 9. | 48.8 | 51.2 | 8.2219 | 0.1216 |
| 10. | 45.9 | 54.1 | 8.1940 | 0.1220 |
| Special. | 43.3 | 56.7 | 8.1209 | 0.1232 |
| Special. | 40.6 | 59.4 | 8.0622 | 0.1241 |
| H. | 40.5 | 59.5 | 8.0511 | 0.1242 |
| 12. | 37.0 | 63.0 | 8.0362 | 0.1244 |
| 13. | 35.0 | 65.0 | 7.9803 | 0.1253 |
| 14. | 34.0 | 66.0 | 7.9540 | 0.1257 |
| 15. | 32.0 | 68.0 | 7.9071 | 0.1265 |
| Special. | 29.0 | 71.0 | 7.7936 | 0.1284 |
| 16. | 27.8 | 72.2 | 7.7305 | 0.1294 |
| 17. | 18.3 | 81.7 | 7.3912 | 0.1353 |
| 18. | 18.0 | 82.0 | 7.3280 | 0.1367 |
| 19. | 16.9 | 83.1 | 7.1421 | 0.1401 |
| 20. | 15.6 | 84.4 | 7.1647 | 0.1396 |
| 21. | 13.58 | 86.42 | 6.9732 | 0.1434 |
| 22. | 8.3 | 91.7 | 7.4413 | 0.1344 |
| Special. | 7.8 | 92.2 | 7.4292 | 0.1346 |
| 23. | 2.8 | 97.2 | 7.1824 | 0.1393 |
| 24. | 2.0 | 98.0 | 7.1930 | 0.1390 |

Table XV.

delta range.

| Alloy. | | | | |
|---|---|---|---|---|
| Per cent Cu. | Per cent Zn. | Quenching medium. | Density. | Specific Volume. |
| 29.0 | 71.0 | cast | 7.7790 | 0.1286 |
| 29.0 | 71.0 | annealed | 7.7936 | 0.1284 |
| 29.0 | 71.0 | quenched | 7.7305 | 0.1294 |

## Table XVI.

Quenching Experiments.

| Alloy. Per cent Cu. | Per cent Zn. | Quenching medium. | Density. | Specific Volume. | Annealed Value of Specific Volume. |
|---|---|---|---|---|---|
| 60.1 | 39.9 | iced brine | 8.3892 | 0.1192 | 0.1195 |
| 53.4 | 46.6 | iced brine | 8.3737 | 0.1195 | |
| 53.4 | 46.6 | iced brine | 8.3624 | 0.1196 | 0.1205 |
| 53.4 | 46.6 | iced brine | 8.3611 | 0.1196 | |
| 53.4 | 46.6 | water | 8.3585 | 0.1197 | |
| 53.4 | 46.6 | water | 8.3549 | 0.1197 | 0.1205 |
| 53.4 | 46.6 | water | 8.3442 | 0.1198 | |
| 53.0 | 47.0 | water | 8.3368 | 0.1199 | - |
| 48.8 | 51.2 | water | 8.2258 | 0.1216 | 0.1217 |
| 45.9 | 54.1 | water | 8.1940 | 0.1220 | 0.1220 |

Table XVII.

| Cast Mark. | Per Cent Copper by weight. | Per cent Zinc by weight. | Shore Hardness Number. (Magnifier Hammer). |
|---|---|---|---|
| 2 | 90.0 | 10.0 | 15.5 |
| 3 | 85.0 | 15.0 | 16 |
| 4 | 80.0 | 20.0 | 16 |
| 5 | 76.0 | 24.0 | 16.5 |
| 6 | 67.4 | 32.6 | 17.0 |
| D | 60.1 | 39.9 | 20 |
| 7 | 56.0 | 44.0 | 22 |
| 8 | 53.4 | 46.6 | 24 |
| 9 | 48.8 | 51.2 | 26 |
| 10. | 45.9 | 54.1 | 39 |
| Special. | 39.0 | 61.0 | 67 |
| 12. | 37.0 | 63.0 | 68½ |
| 13. | 35.0 | 65.0 | 60 |
| 15. | 32.0 | 68.0 | 70 |
| Special. | 29.0 | 71.0 | 29 |
| 17. | 18.3 | 81.7 | 12 |
| Special. | 18.0 | 82.0 | 21 |
| 19. | 16.9 | 83.1 | 20 |
| Special. | 15.6 | 84.4 | 17 |
| 21. | 13.58 | 86.42 | 18 |
| Special. | 13.5 | 86.5 | 18 |
| Special. | 11.6 | 88.4 | 18 |
| | 8.3 | 91.7 | 28 |
| | 7.5 | 92.5 | 21 |
| 24. | 2.8 | 97.2 | 18 |
| 25. | 2.0 | 98.0 | 22 |

Table XVIII.

| Per Cent Copper by weight. | Per cent Zinc by weight. | Treatment. | Shore Hardness Number. (Magnifier Hammer). |
|---|---|---|---|
| 53.4 | 46.6 | As cast. | 27 |
| 53.4 | 46.6 | Annealed | 24 |
| 53.4 | 46.6 | Quenched | 31 |

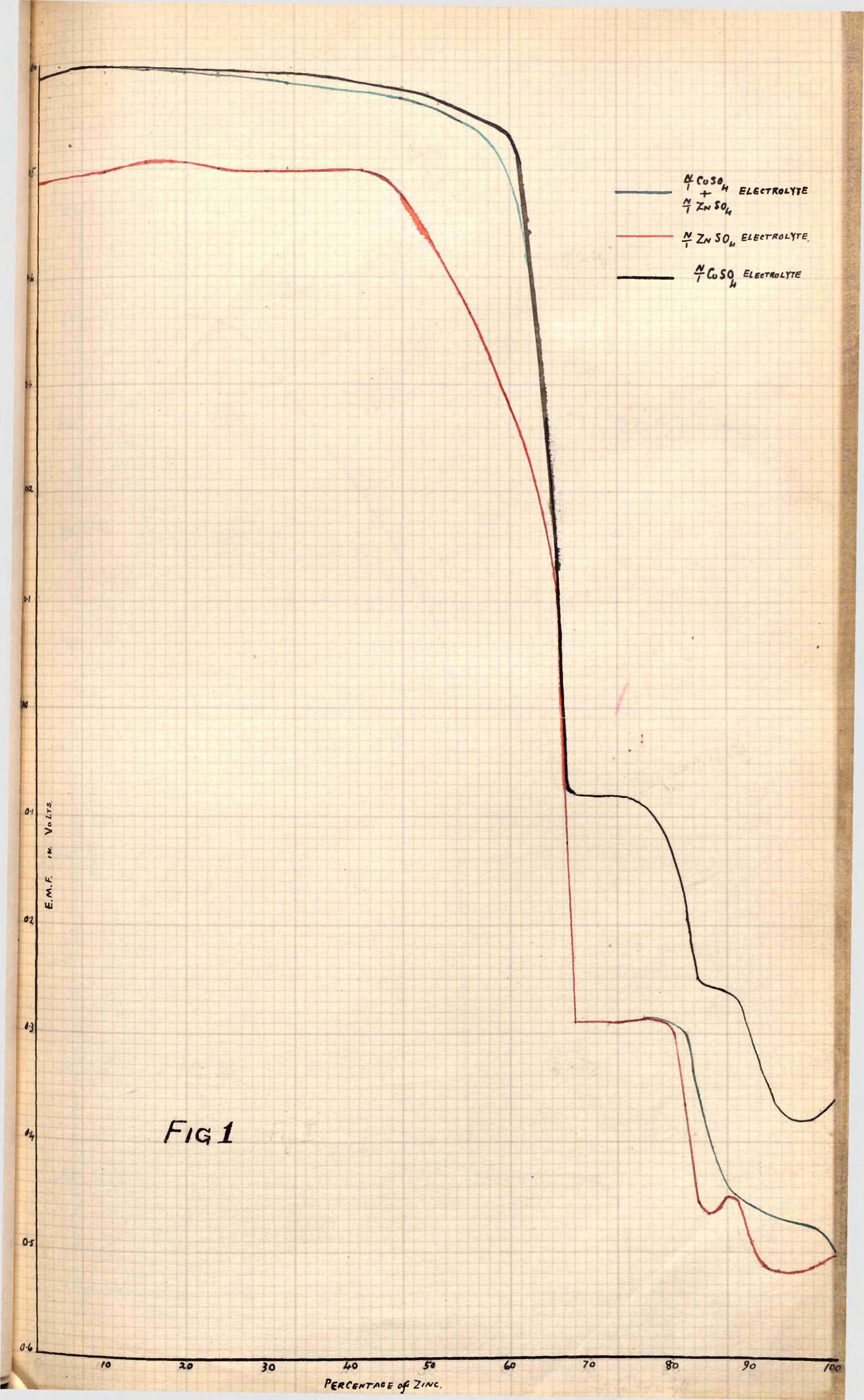

$\frac{N}{1}$ $CuSO_4$ + $\frac{N}{1}$ $ZnSO_4$ ELECTROLYTE
$\frac{N}{1}$ $ZnSO_4$ ELECTROLYTE
$\frac{N}{1}$ $CuSO_4$ ELECTROLYTE
E.M.F. in Volts.
0·6
0·5
0·4
0·3
0·2
0·1
10
20
30
40
50
60
70
80
90
100
Percentage of Zinc.

FIG 1

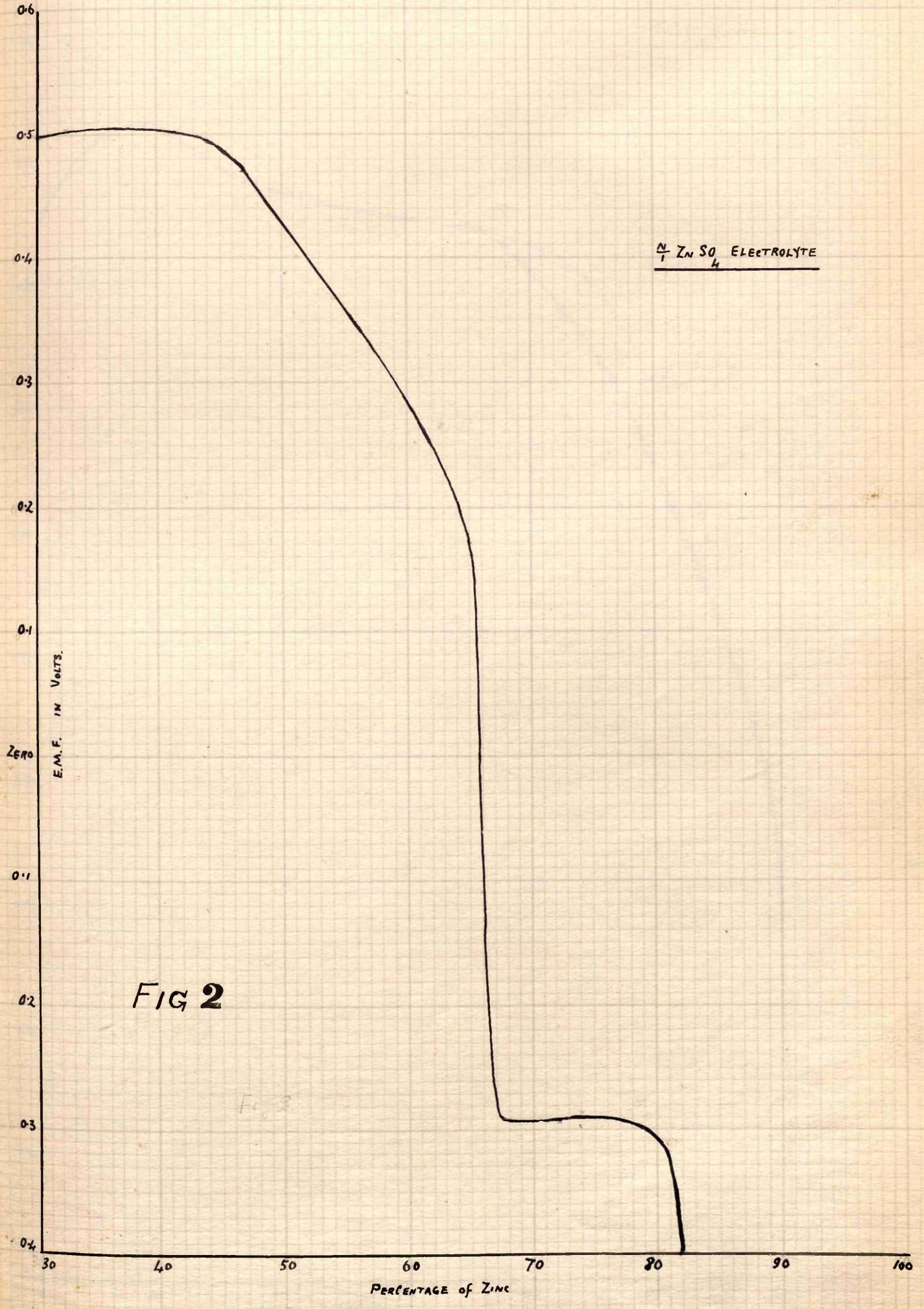

0·6
0·5
0·4
0·3
0·2
0·1
Zero
0·1
0·2
0·3
0·4
E.M.F. in Volts.
30
40
50
60
70
80
90
100
Percentage of Zinc
N/1 Zn SO4 Electrolyte

FIG 2

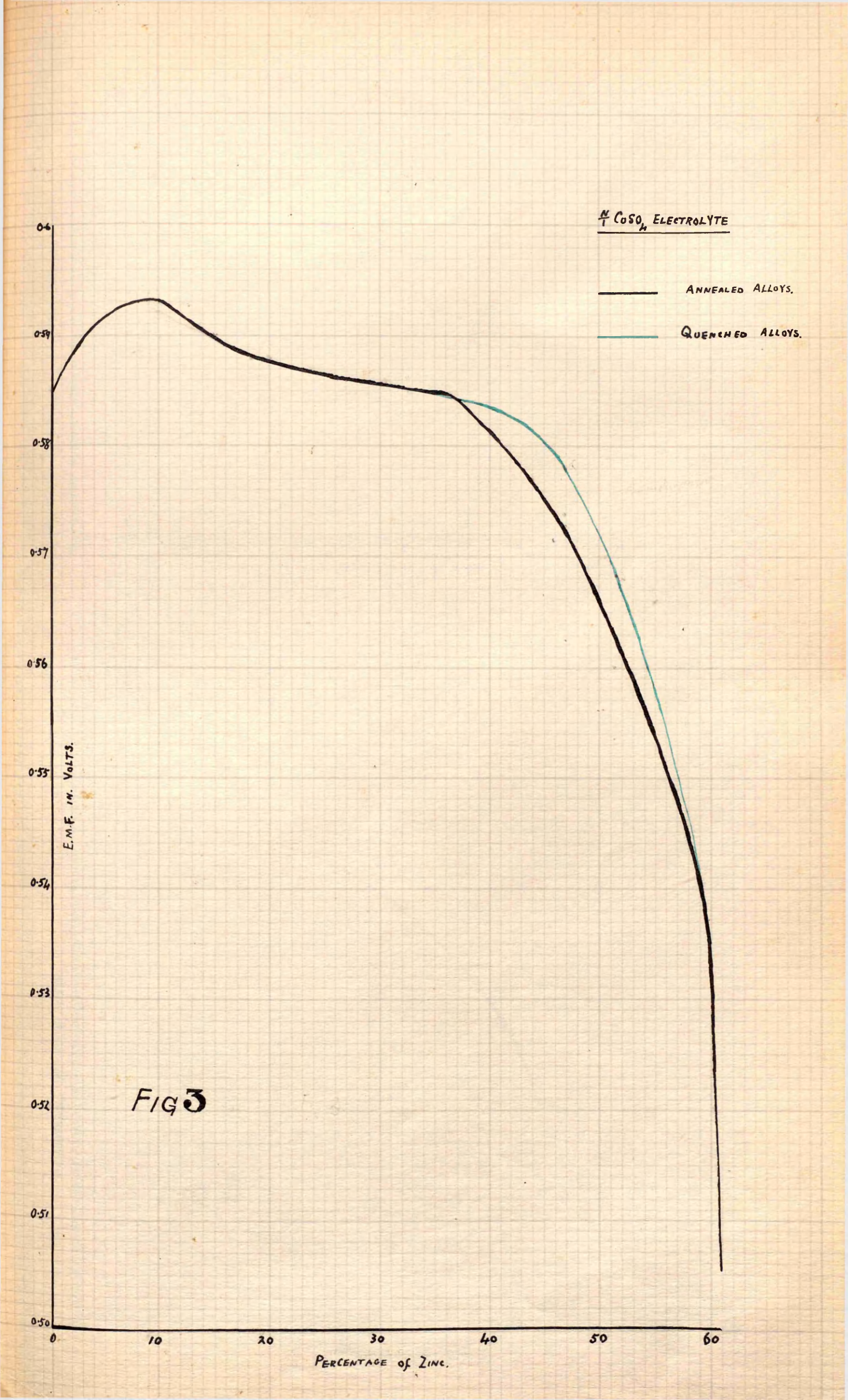

$\frac{N}{1}$ $CoSO_4$ ELECTROLYTE
ANNEALED ALLOYS.
QUENCHED ALLOYS.
0·6
0·59
0·58
0·57
0·56
0·55
0·54
0·53
0·52
0·51
0·50
E.M.F. IN VOLTS.
0
10
20
30
40
50
60
PERCENTAGE of ZINC.

FIG 3

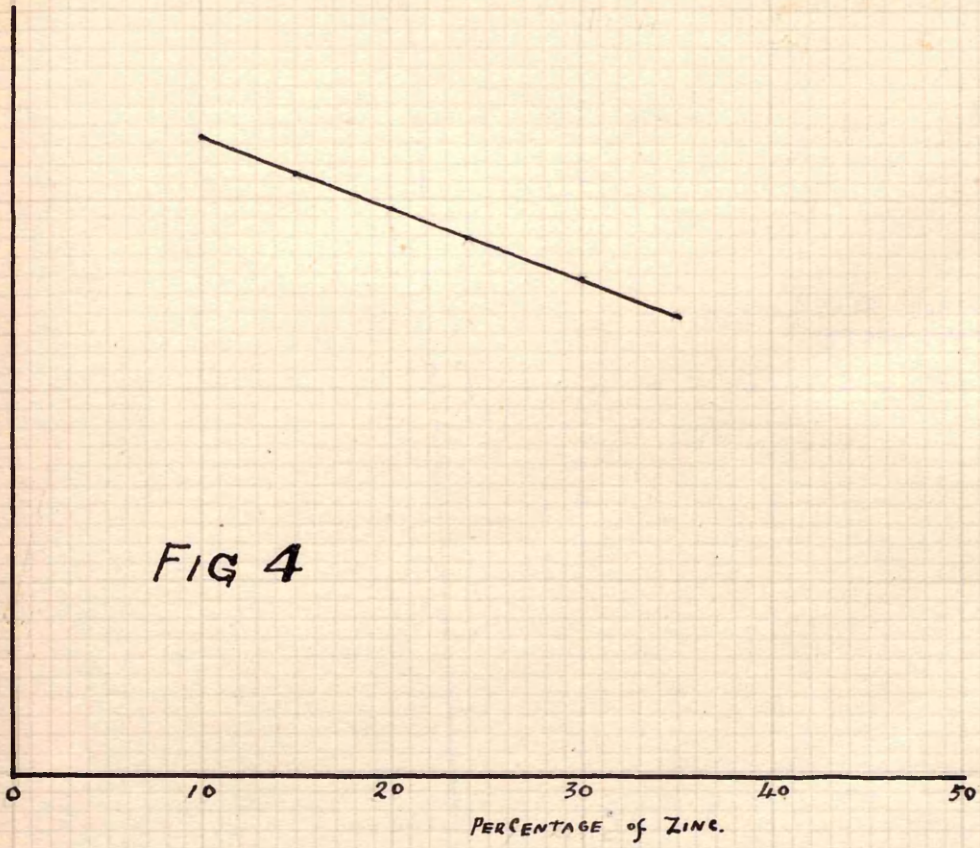

Logarithm of E.M.F Values.
0
10
20
30
40
50
Percentage of Zinc.

FIG 4

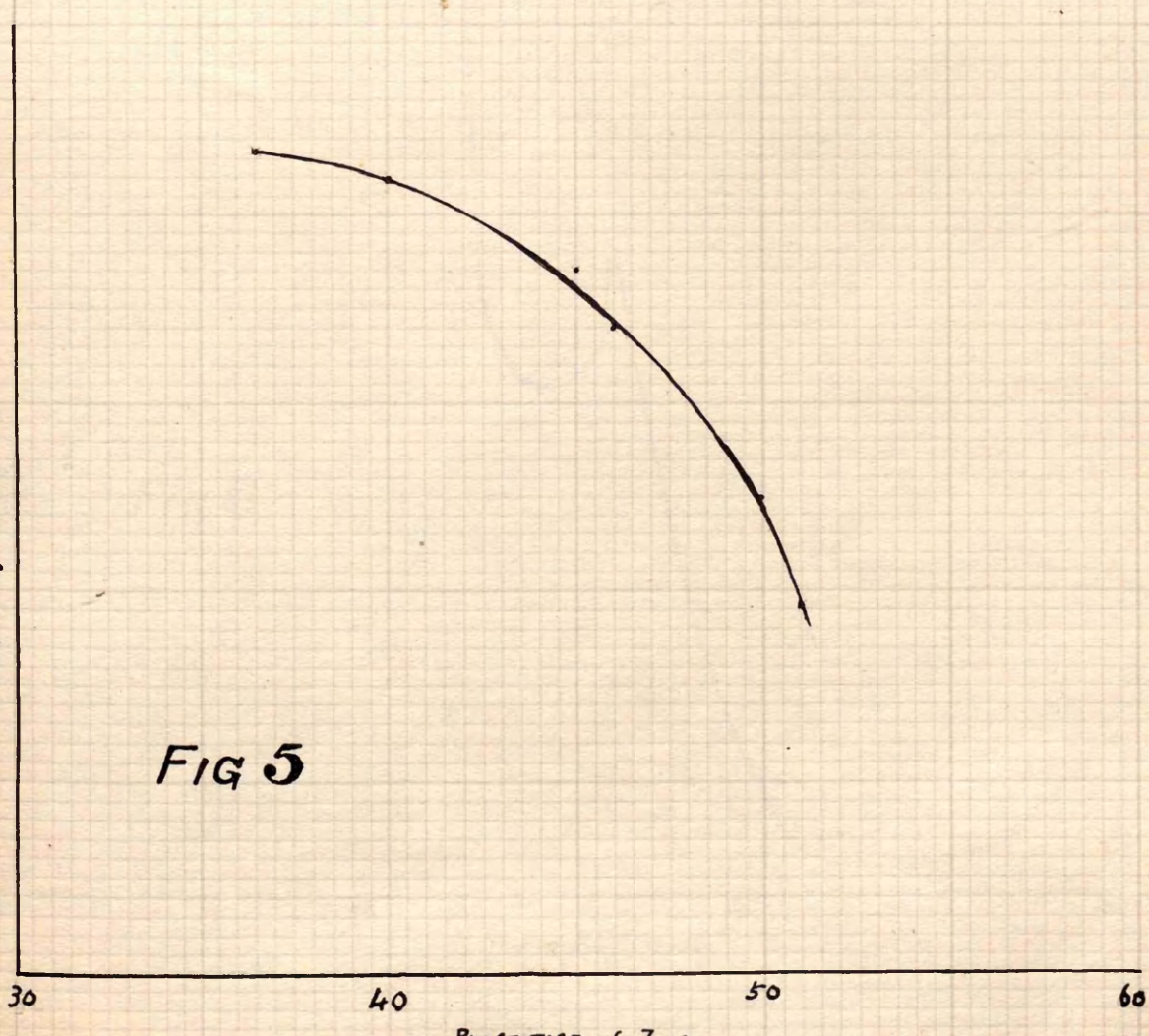

Logarithm of E.M.F. Value
30
40
50
60
Percentage of Zinc.

FIG 5

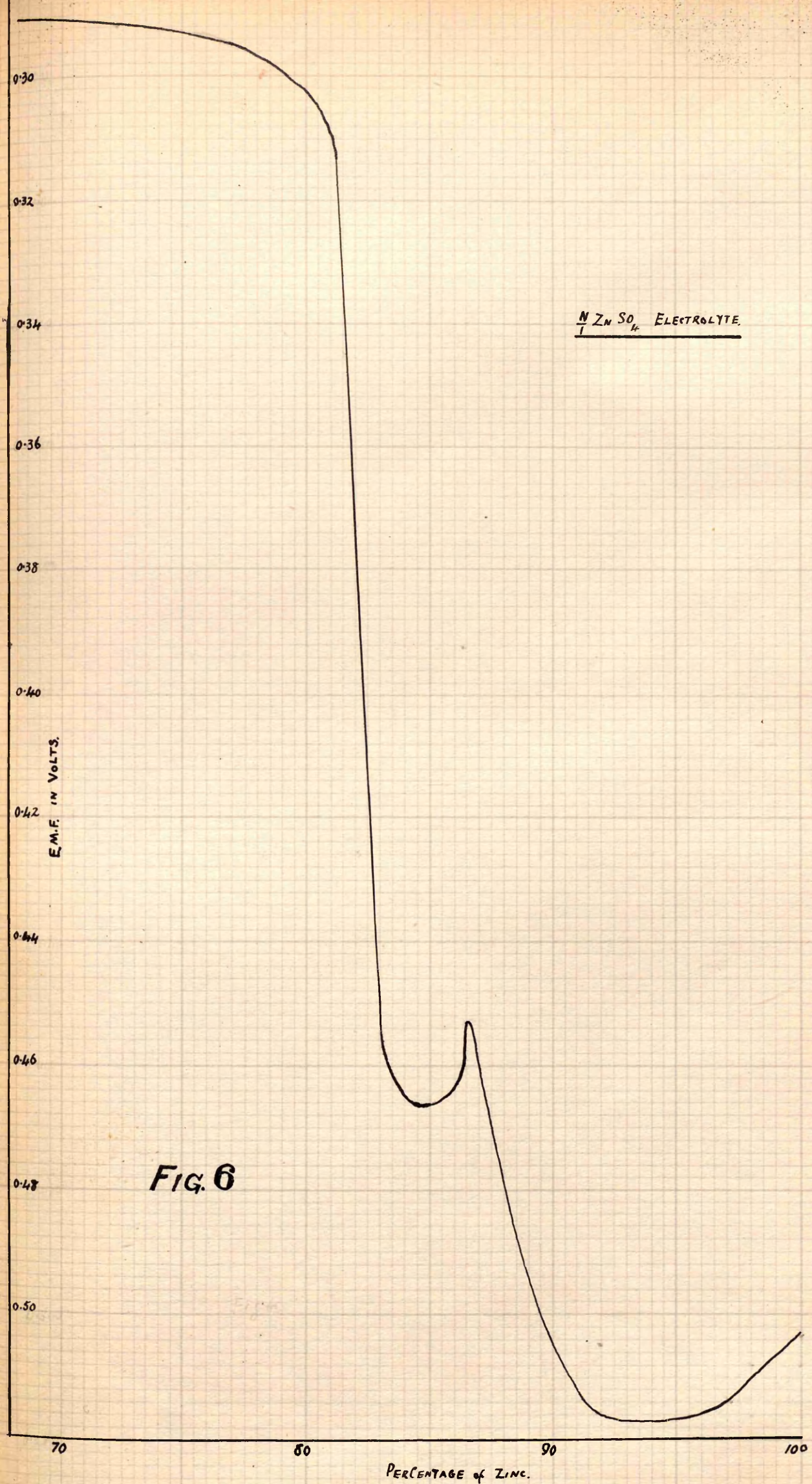

0·30
0·32
0·34
0·36
0·38
0·40
0·42
0·44
0·46
0·48
0·50
E.M.F. IN VOLTS.
N/1 Zn SO4 ELECTROLYTE.
70
80
90
100
PERCENTAGE of ZINC.

FIG. 6

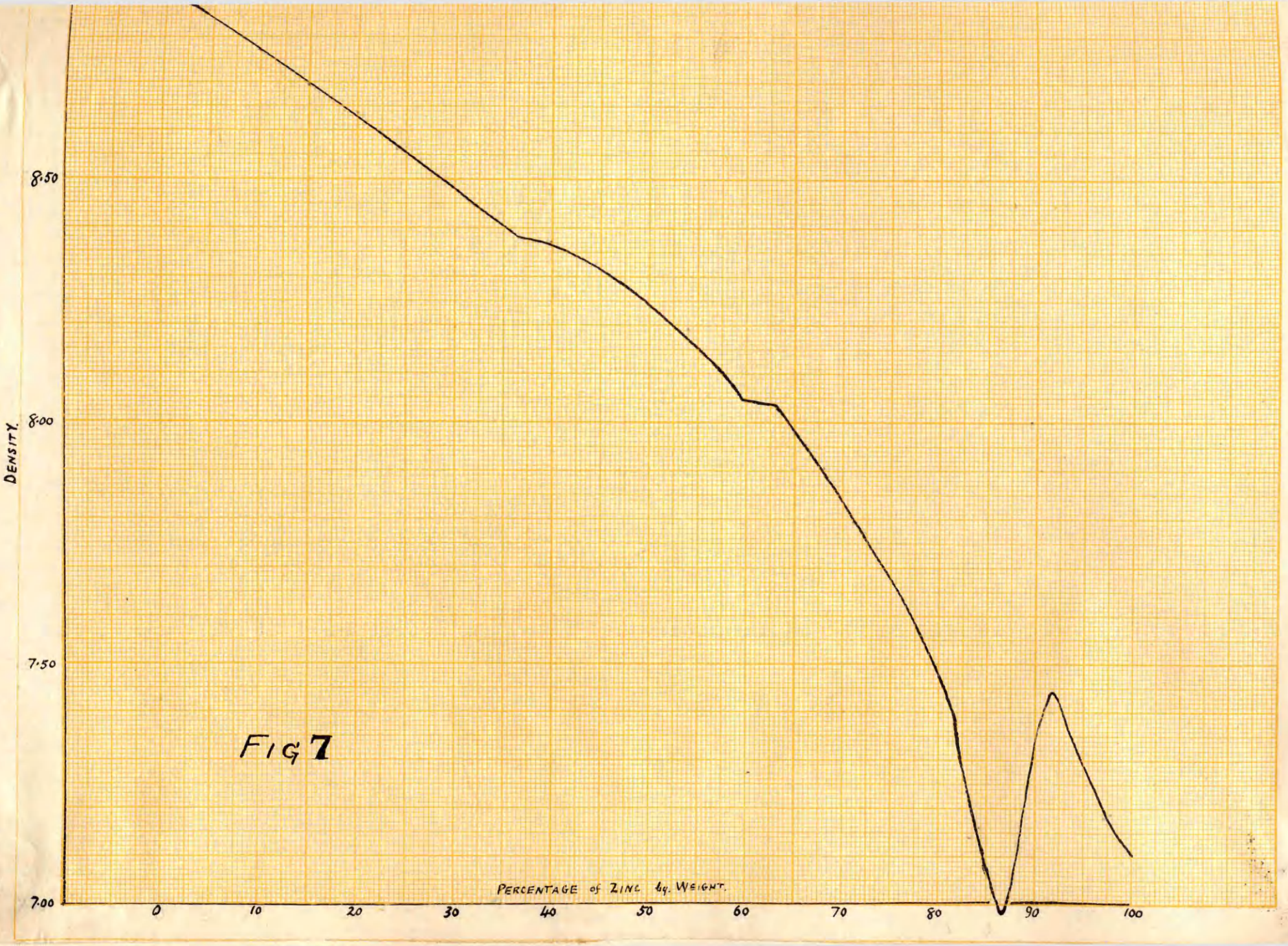
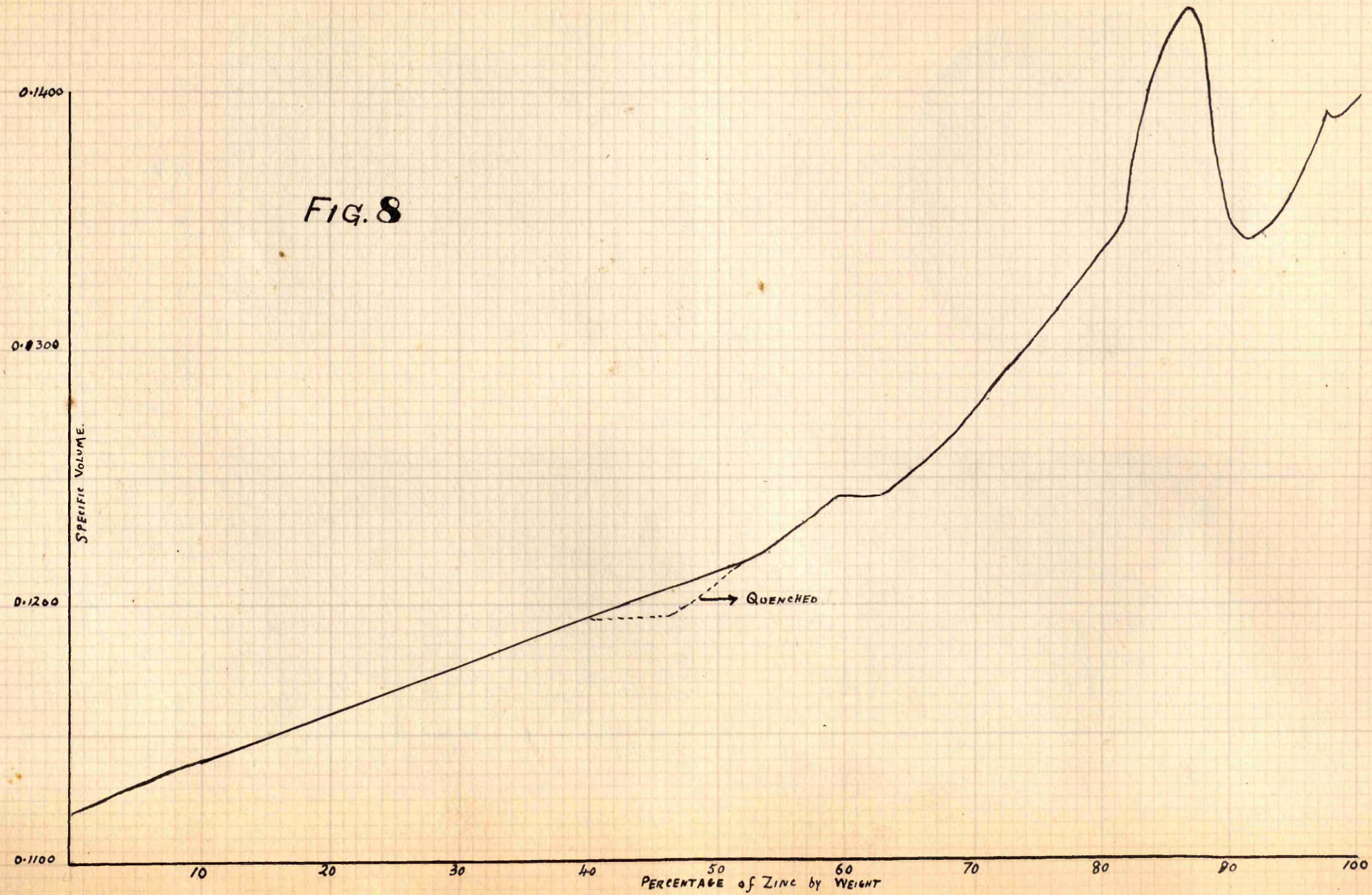

8·50
8·00
7·50
7·00
DENSITY.
0
10
20
30
40
50
60
70
80
90
100
PERCENTAGE of ZINC by WEIGHT.

FIG 7

FIG. 8


0·1400
0·1300
0·1200
0·1100
SPECIFIC VOLUME.
QUENCHED
10
20
30
40
50
60
70
80
90
100
PERCENTAGE of ZINC by WEIGHT

# Cu. Zn. ALLOYS containing 29% Cu.

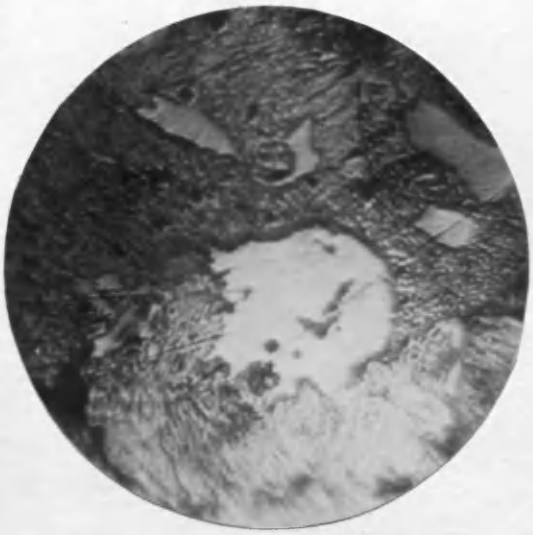
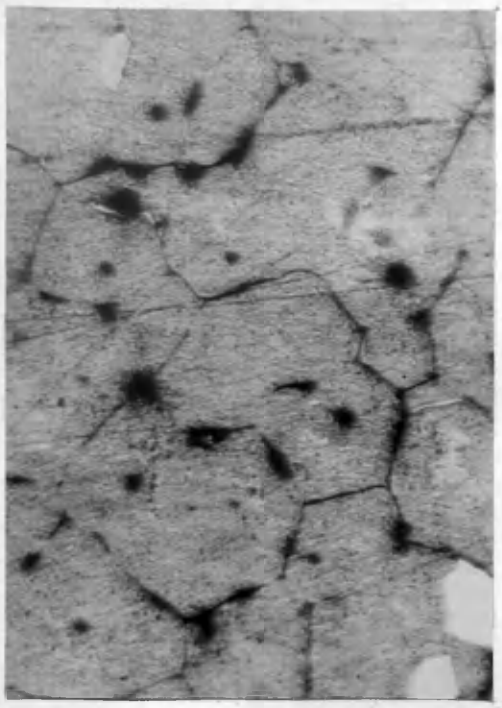


Fig 9 As Cast
X300



Quenched in Iced Brine from 600°C
Fig 10 X150

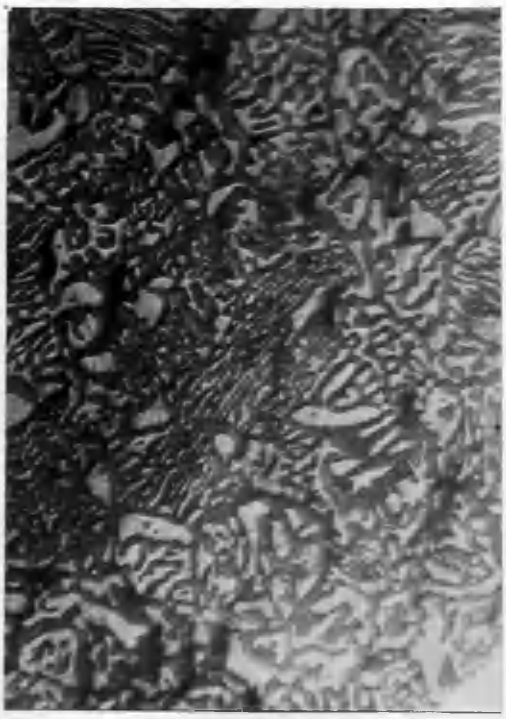


FIG. 11 Quenched in Water from 500°C
X150

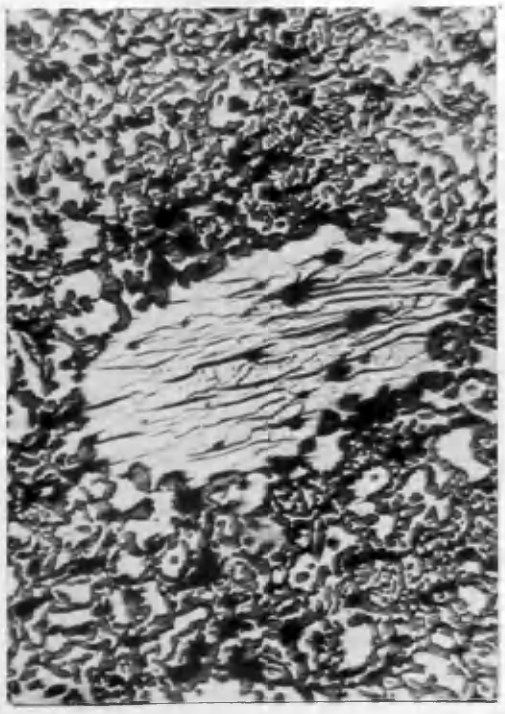


Fig 12. Annealed showing piece of gamma remainder of specimen all eutectiferous
X150

All etched in Chromic Acid

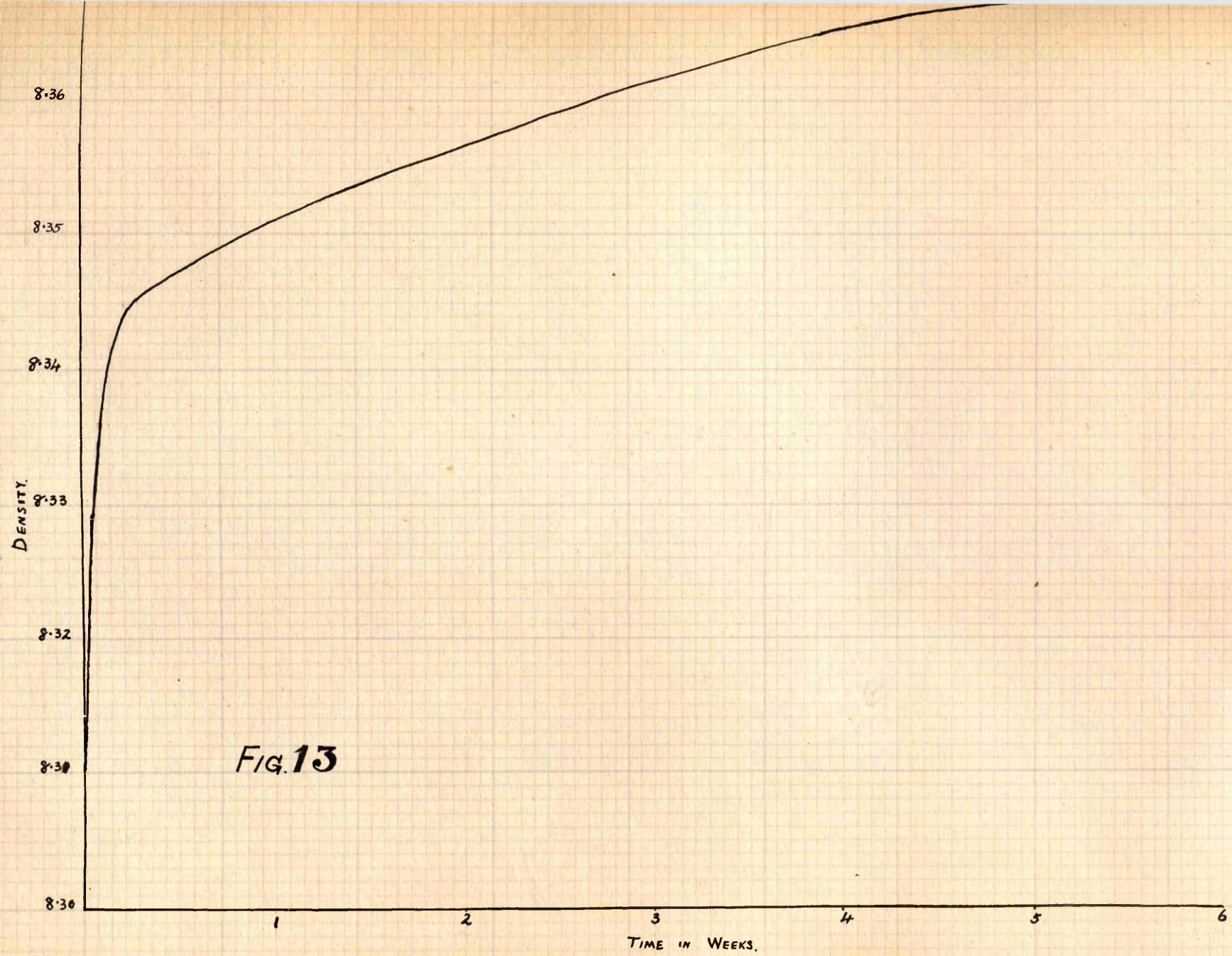



FIG. 13

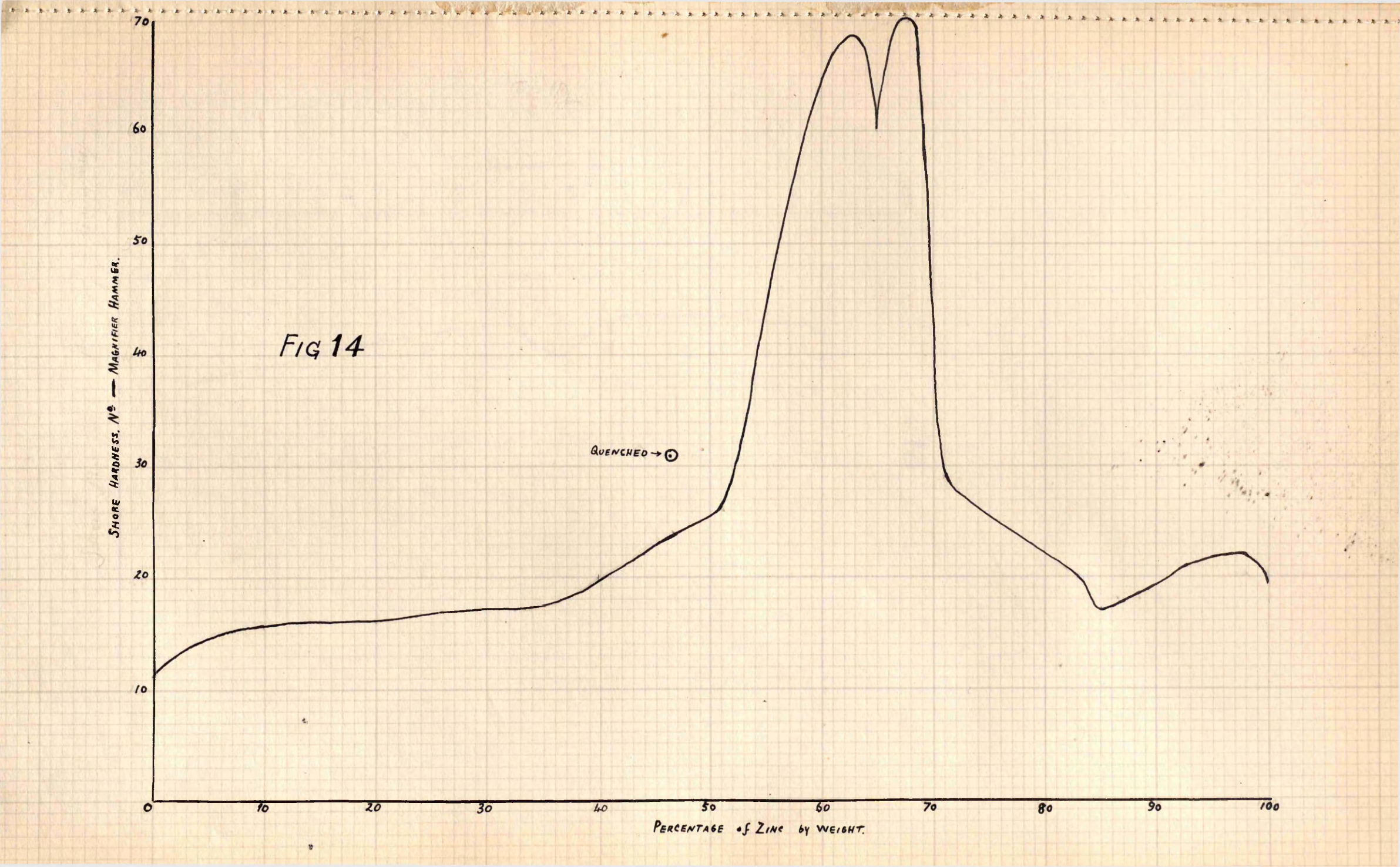
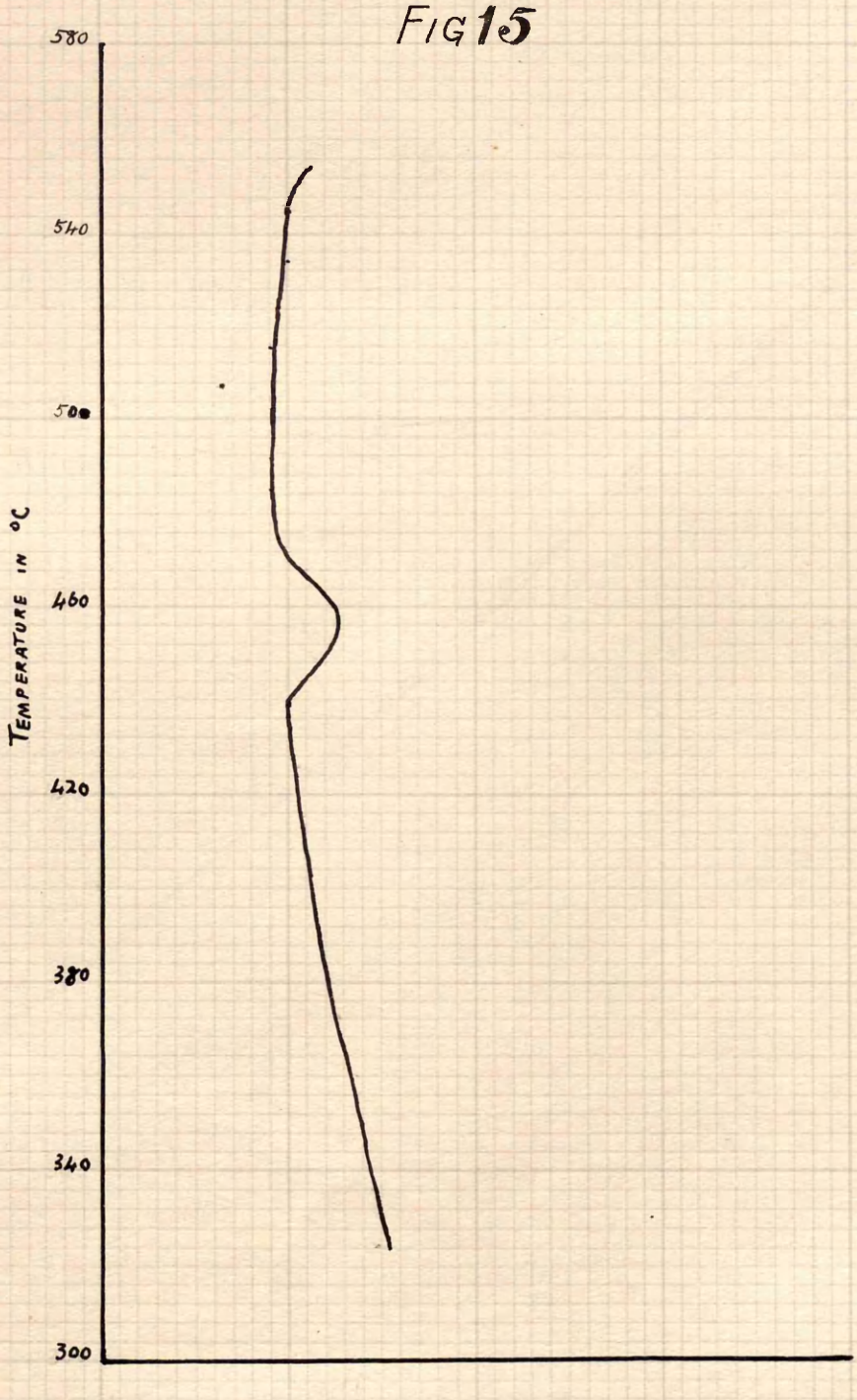


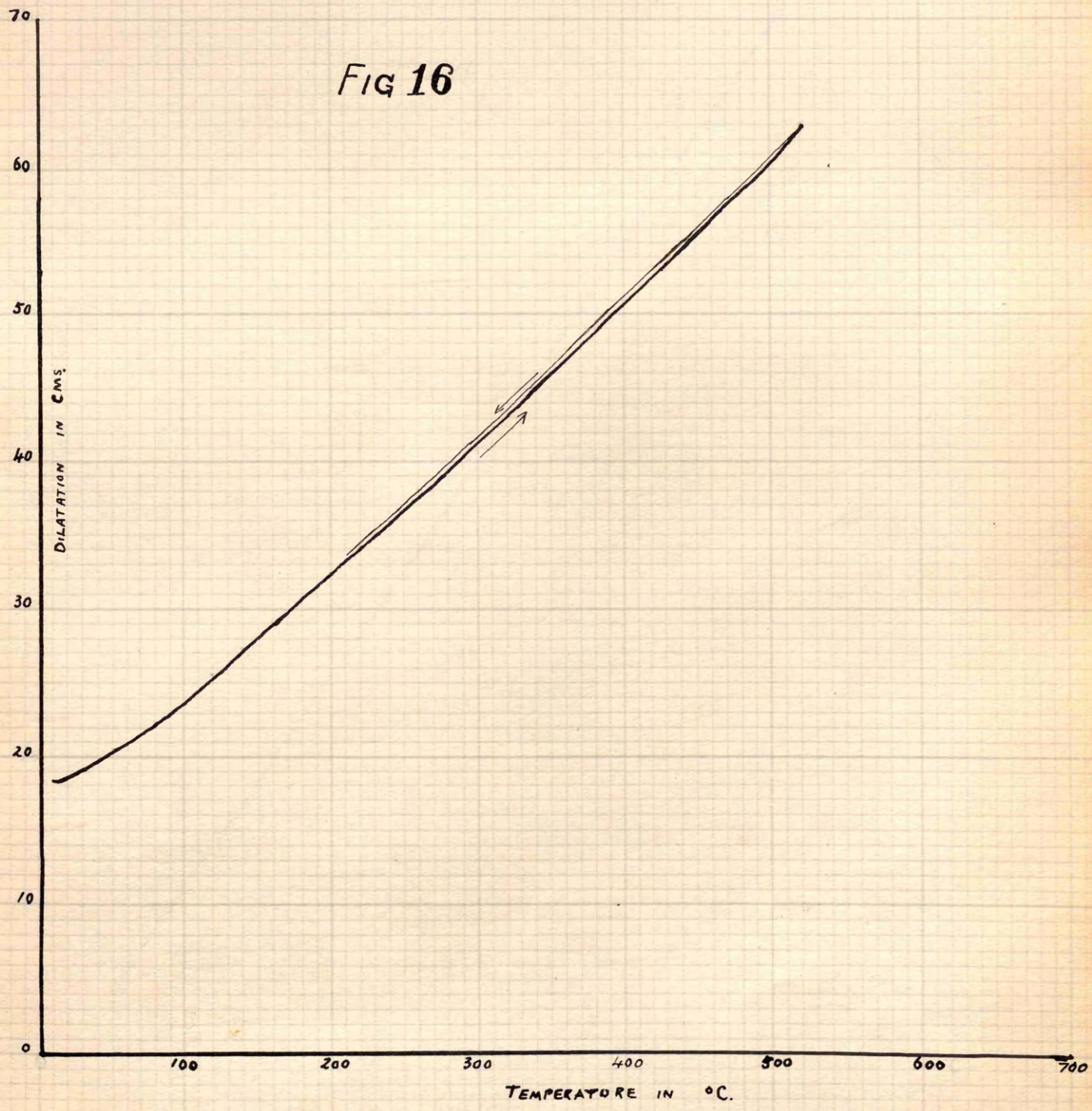
FIG 14
SHORE HARDNESS. Nº. — MAGNIFIER HAMMER.
70
60
50
40
30
20
10
0
QUENCHED →
10
20
30
40
50
60
70
80
90
100
PERCENTAGE of ZINC by WEIGHT.

FIG 15



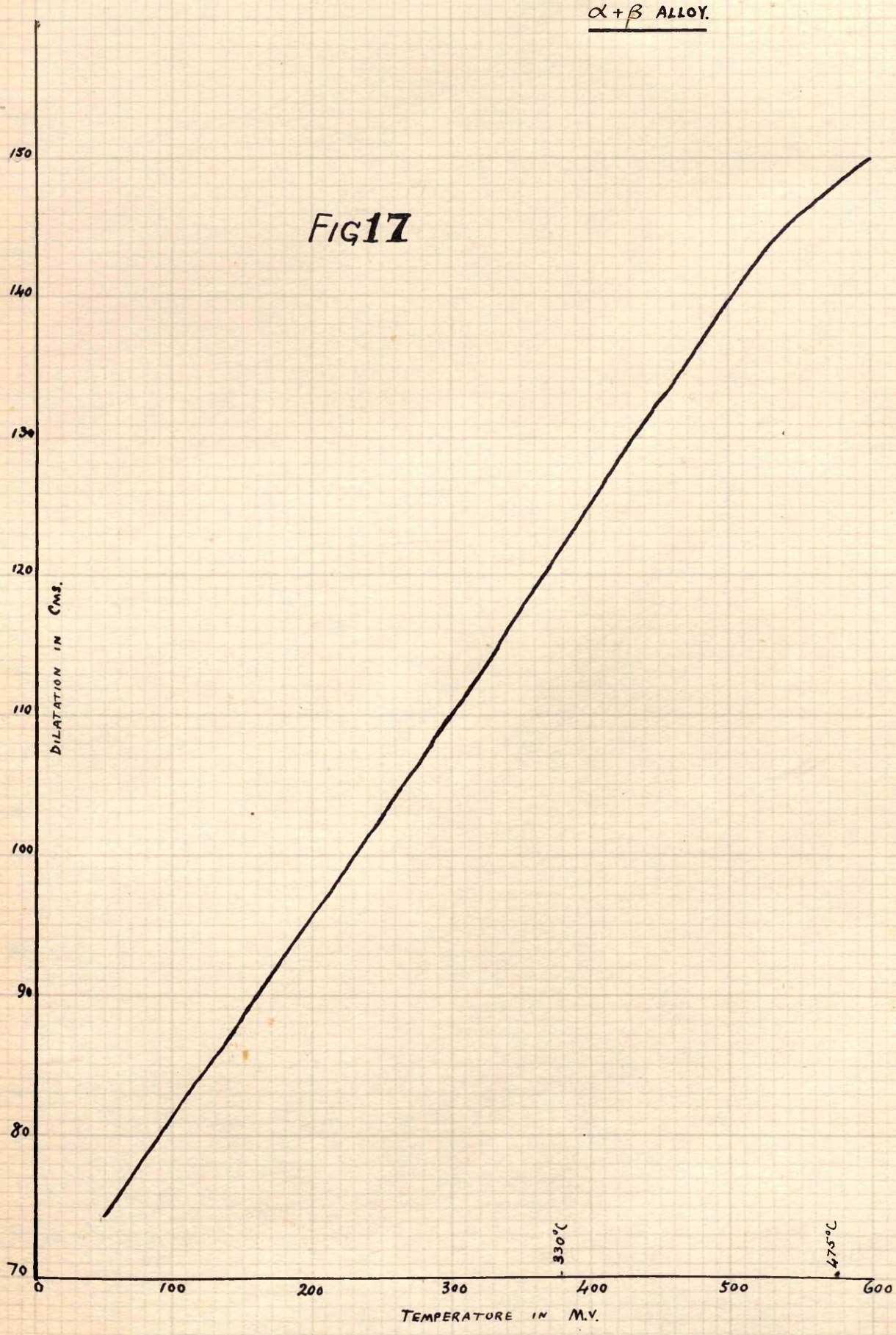
α ALLOY

FIG 16



$\alpha + \beta$ ALLOY.

FIG 17

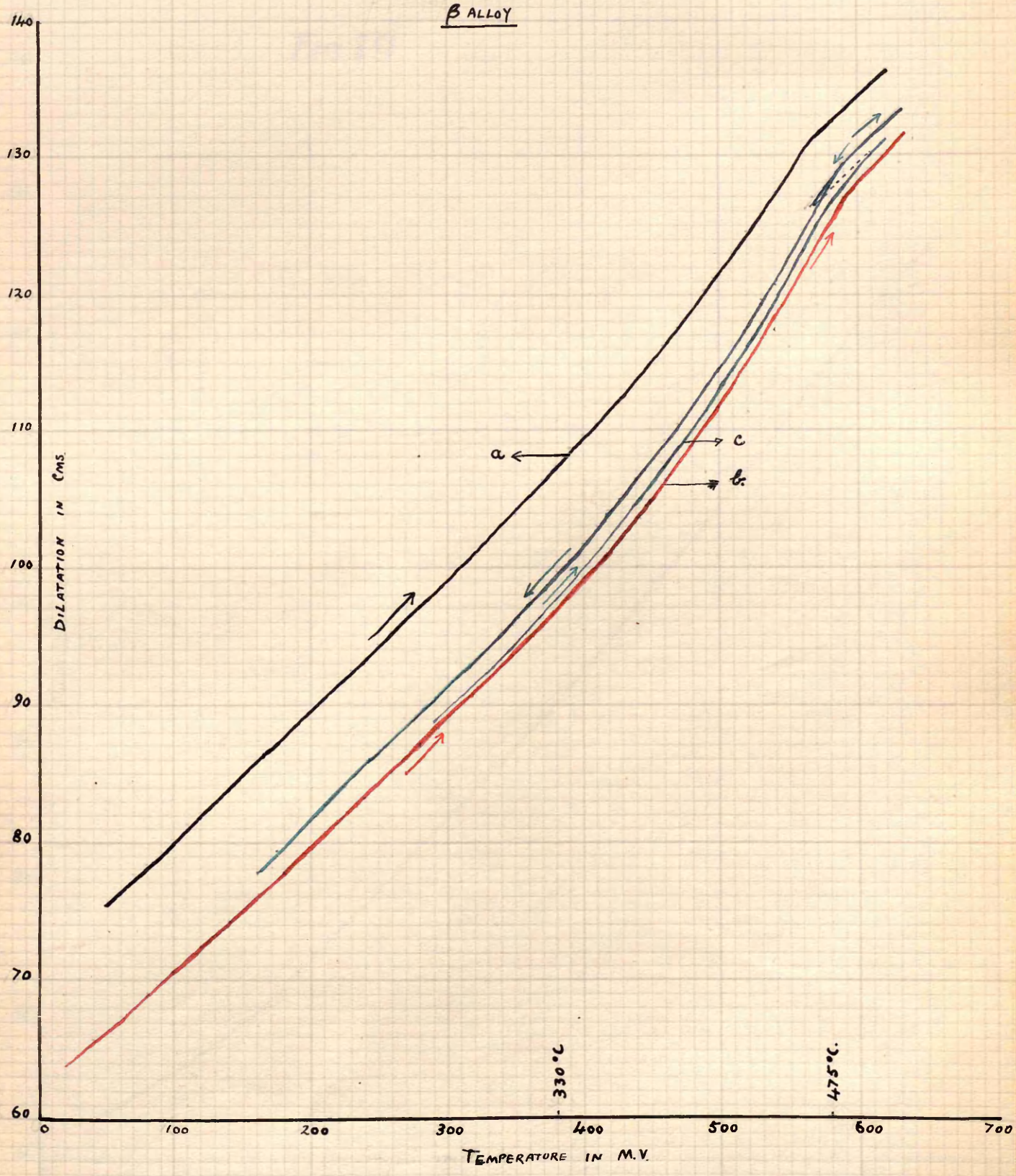


# Fig 18

(b) RATE of HEATING — VERY SLOW

(c) HEATED VERY SLOWLY — SOAKED at 460°C for 3 HOURS.

(a) RATE of HEATING — VERY FAST.



β+γ ALLOY

FIG 19

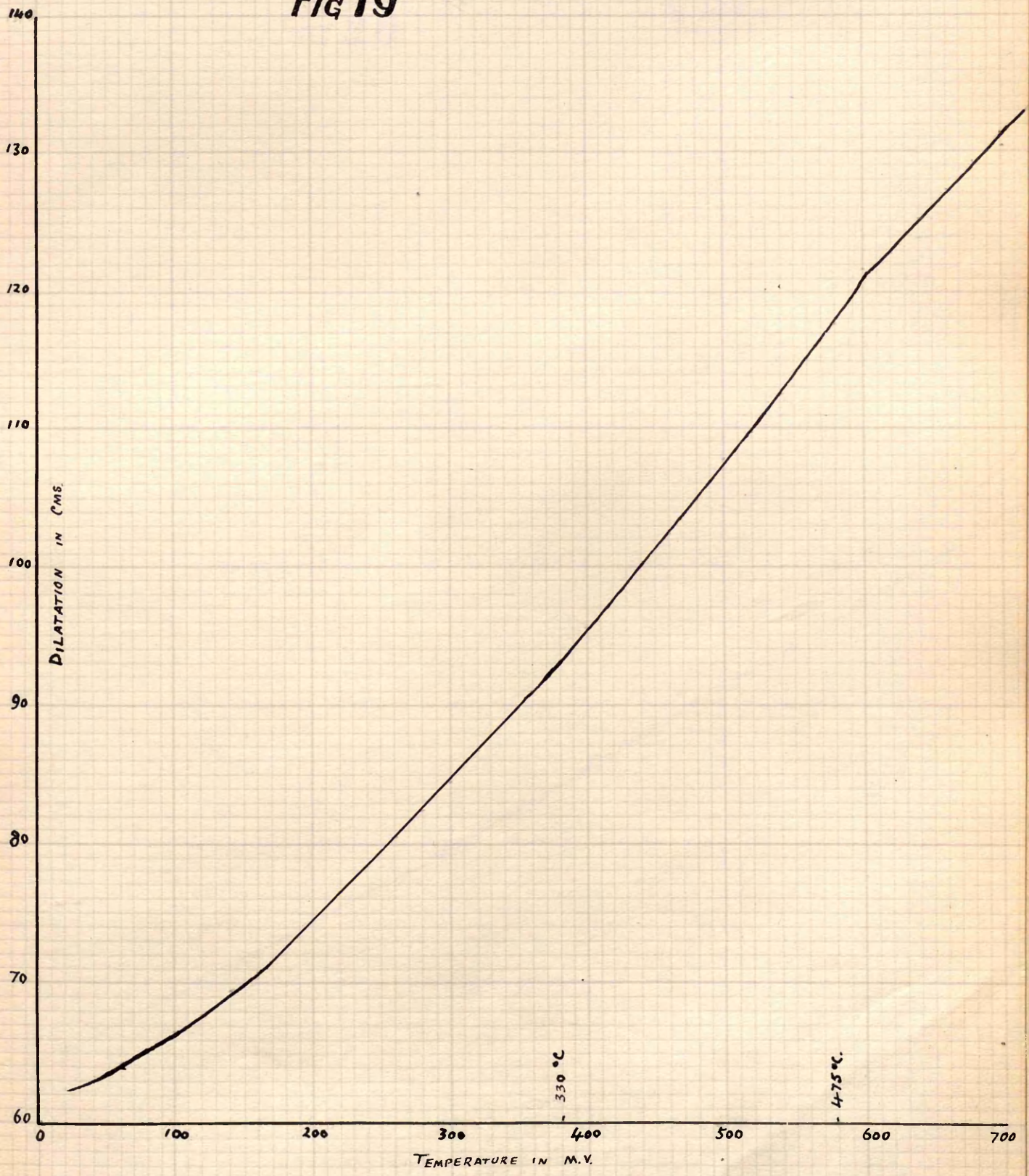


FIG 20

Y ALLOY

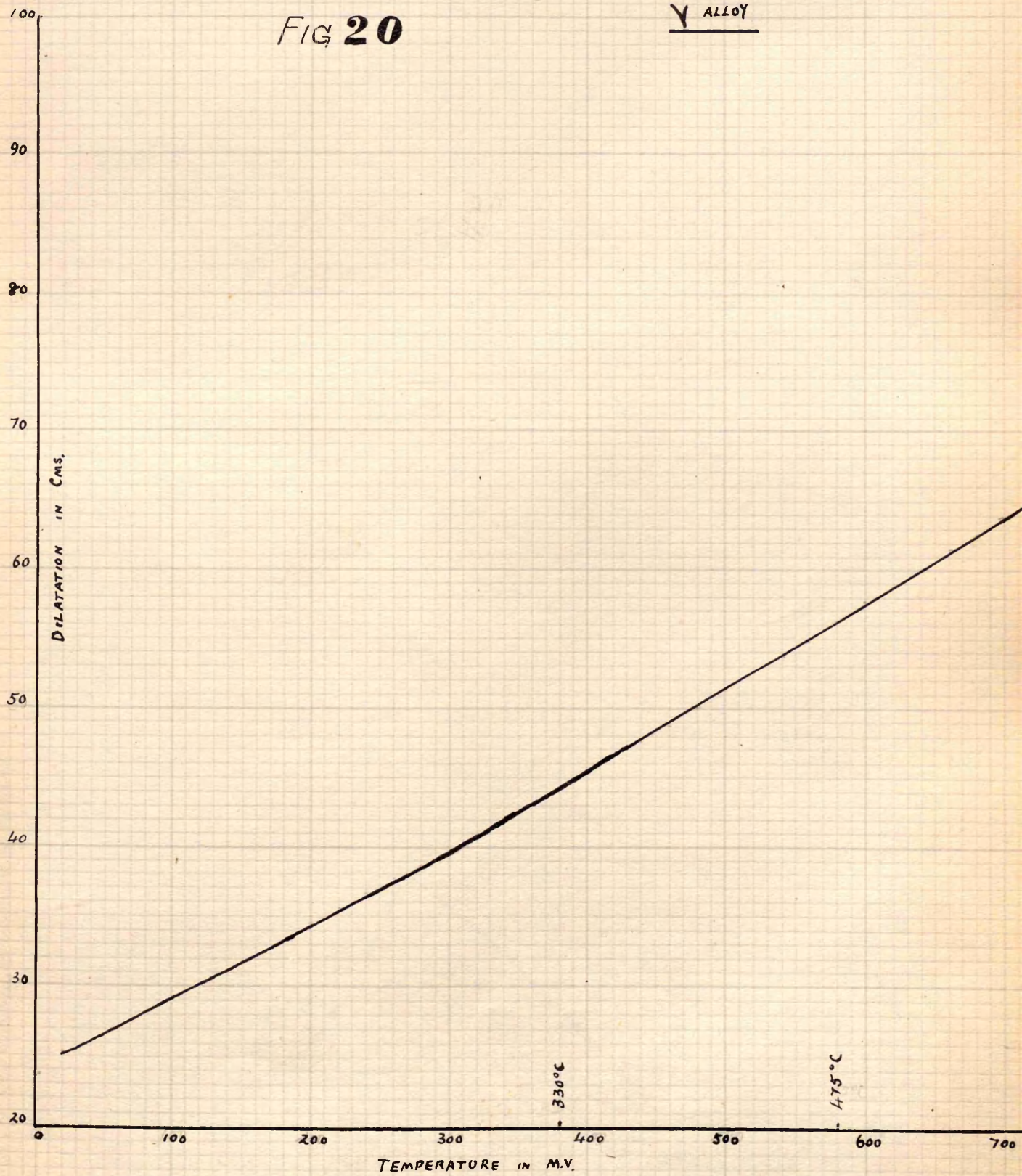


FIG 21

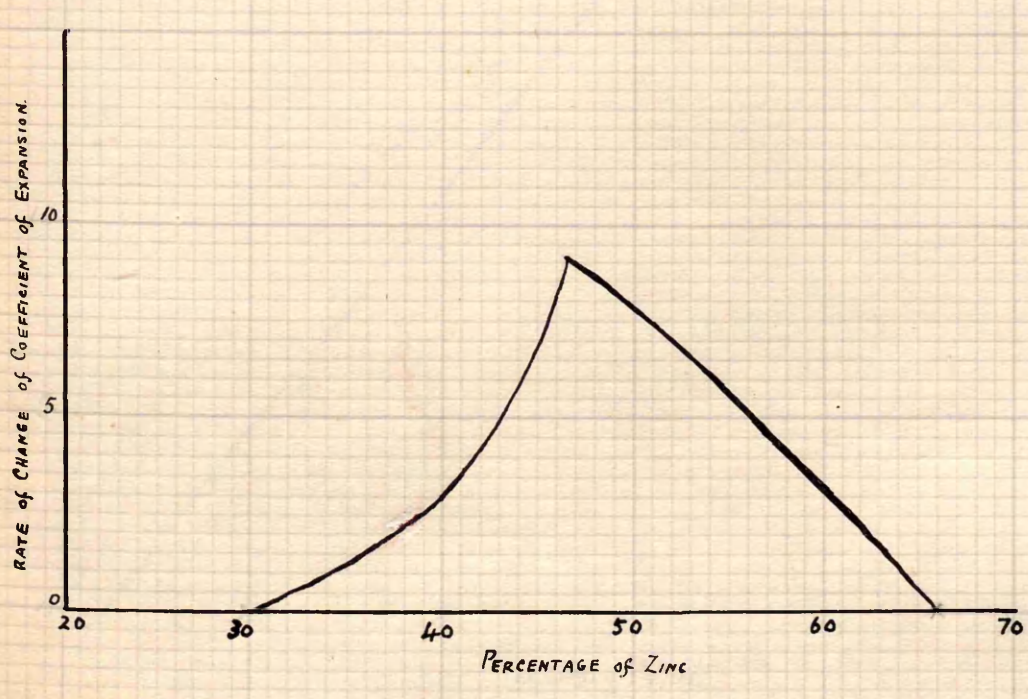
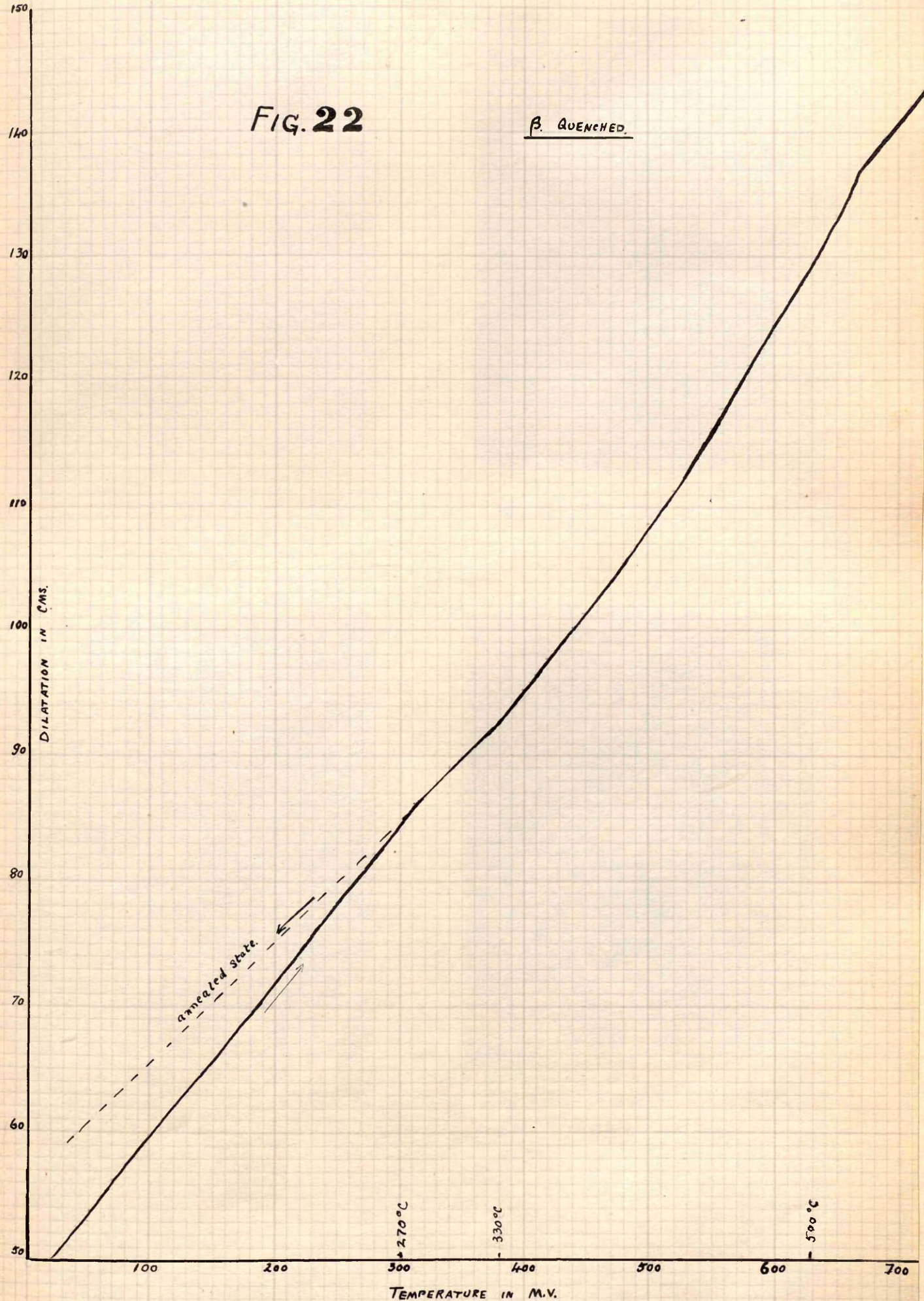

RATE of CHANGE of COEFFICIENT of EXPANSION.
10
5
0
20
30
40
50
60
70
PERCENTAGE of ZINC

FIG. 22

β. QUENCHED.



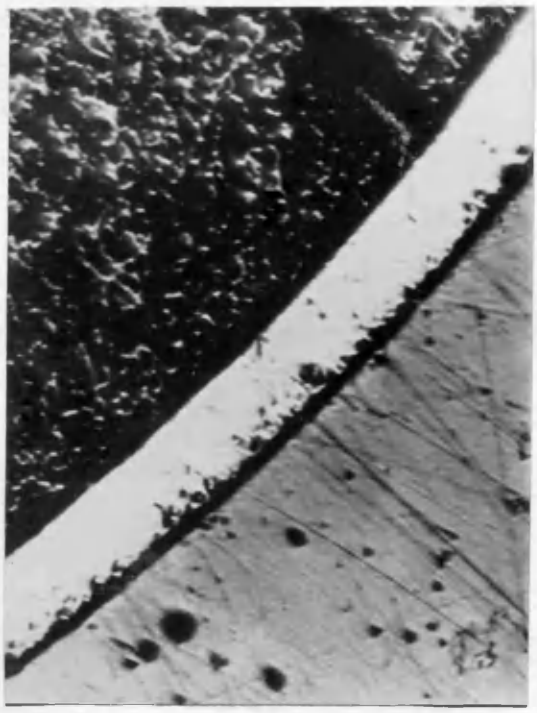


Fig 23 Soaked at 500°C for 4 Days X120

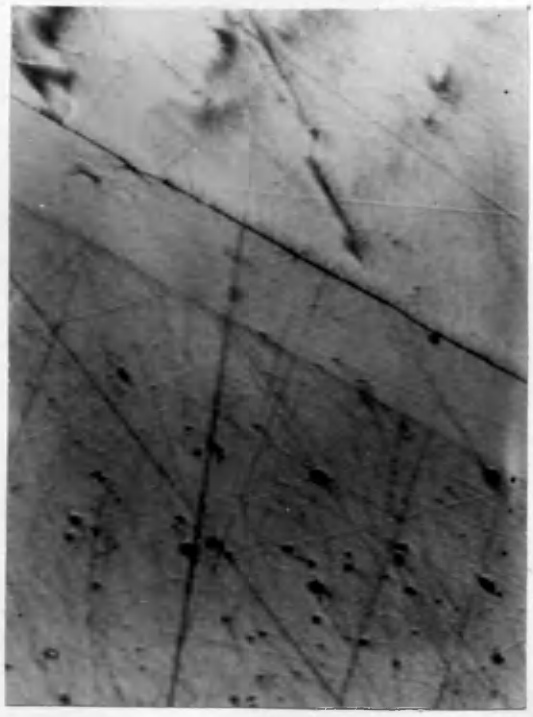


Fig 24 Soaked at 500°C for 5 Days X120

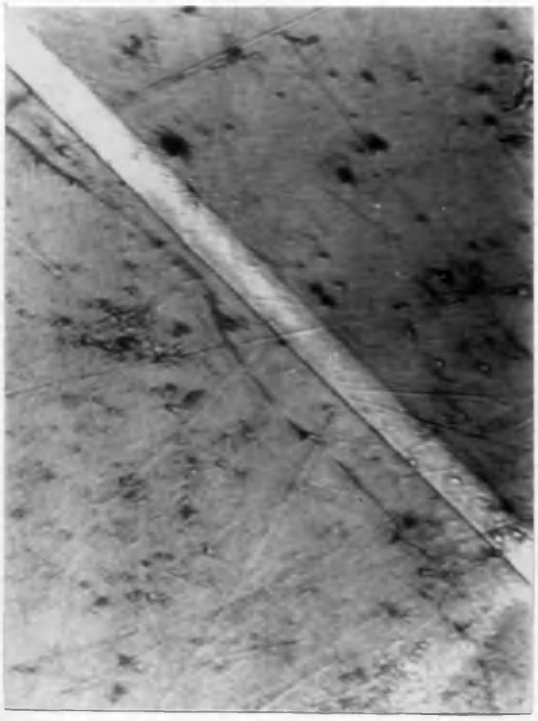


Fig. 25 Soaked at 400°C for 2 Days X120

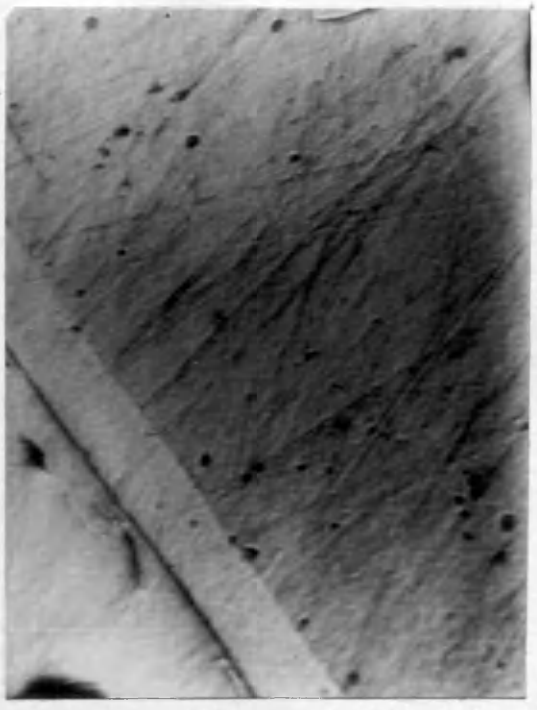


Fig 26 Soaked at 400°C for 4 Days X120

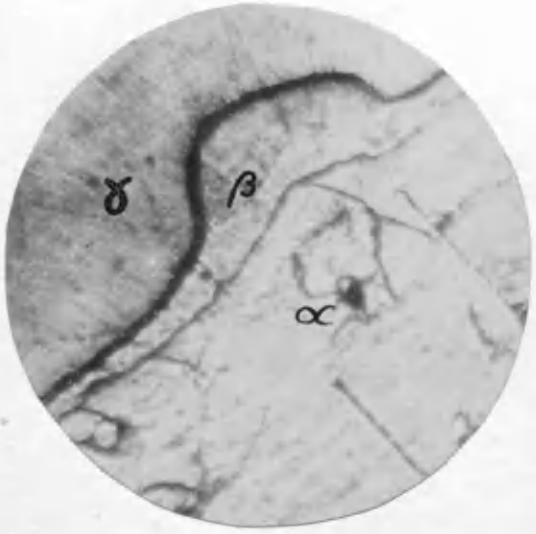



Fig 27. X250

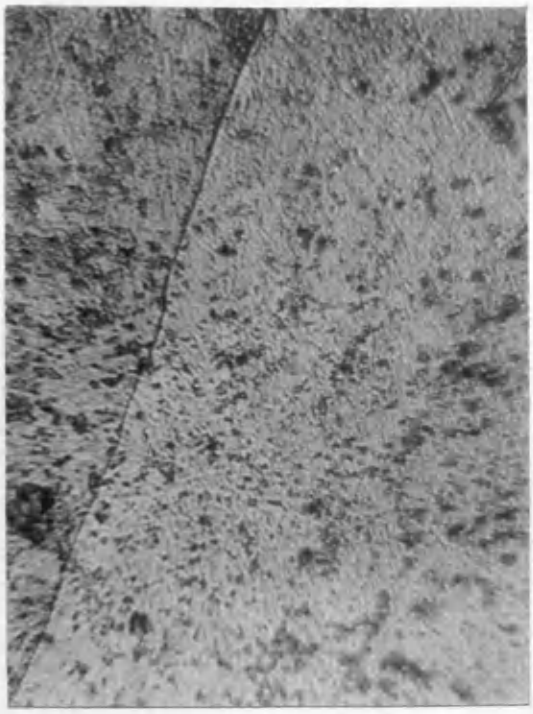


Fig 28. β brass with 0·5% Vanadium X200

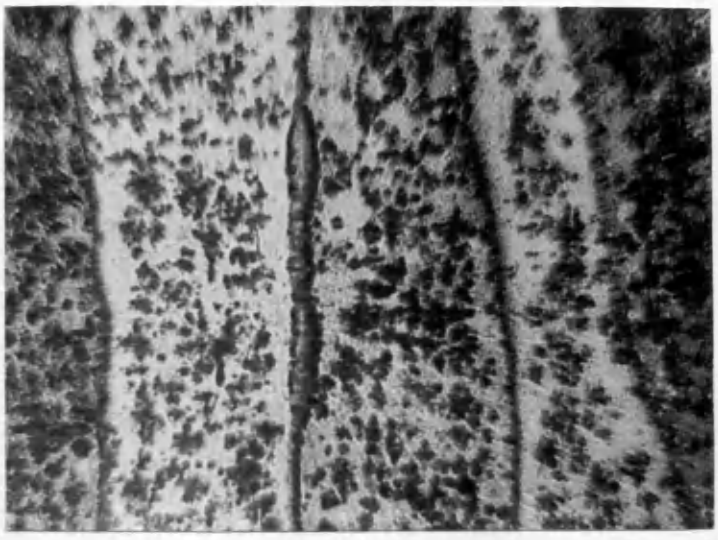


Fig 29. β brass with 1% Tin X120

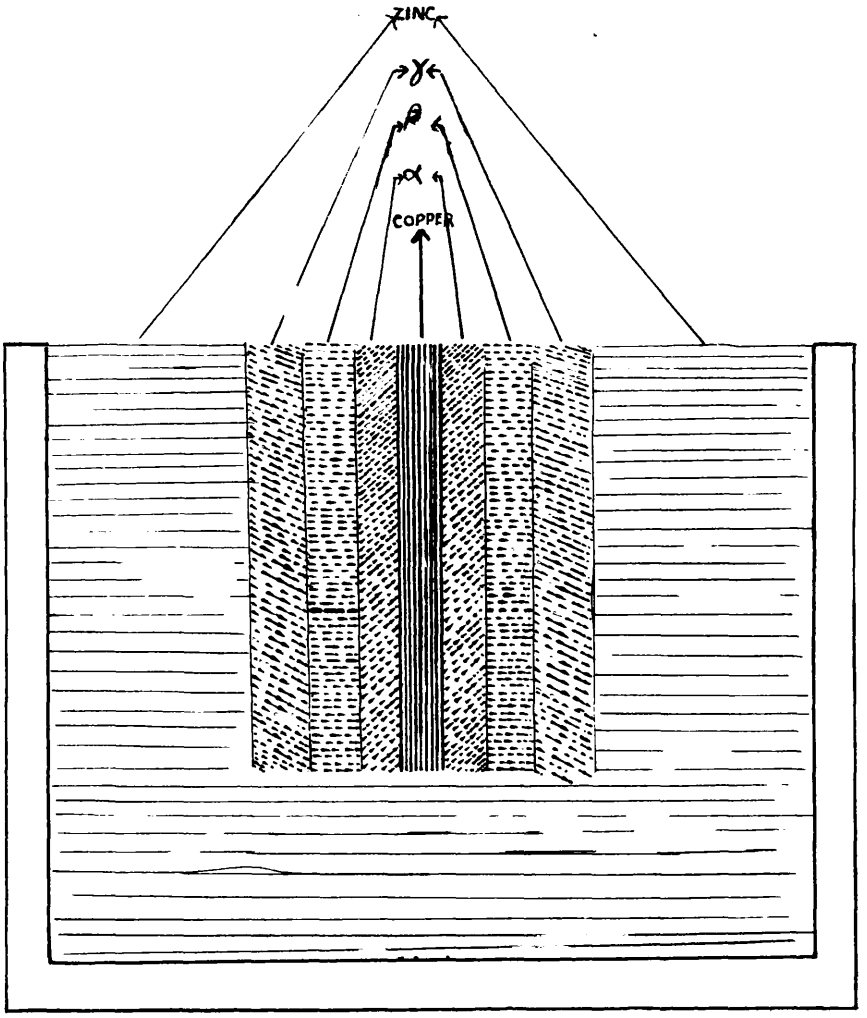



FIG 30

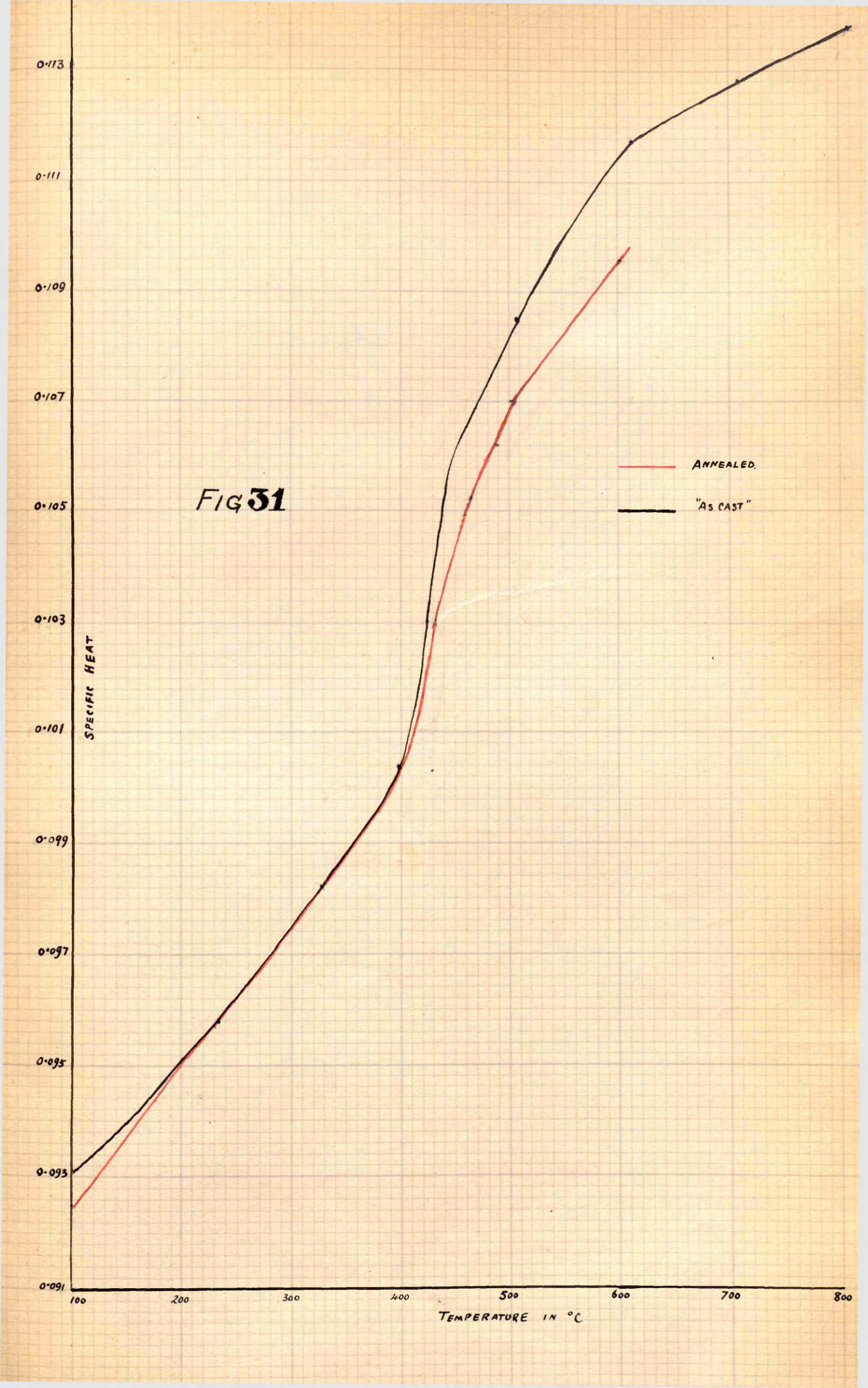

0·113
0·111
0·109
0·107
0·105
0·103
0·101
0·099
0·097
0·095
0·093
0·091
SPECIFIC HEAT
100
200
300
400
500
600
700
800
TEMPERATURE IN °C
ANNEALED.
"AS CAST"

FIG 31

FIG. 32

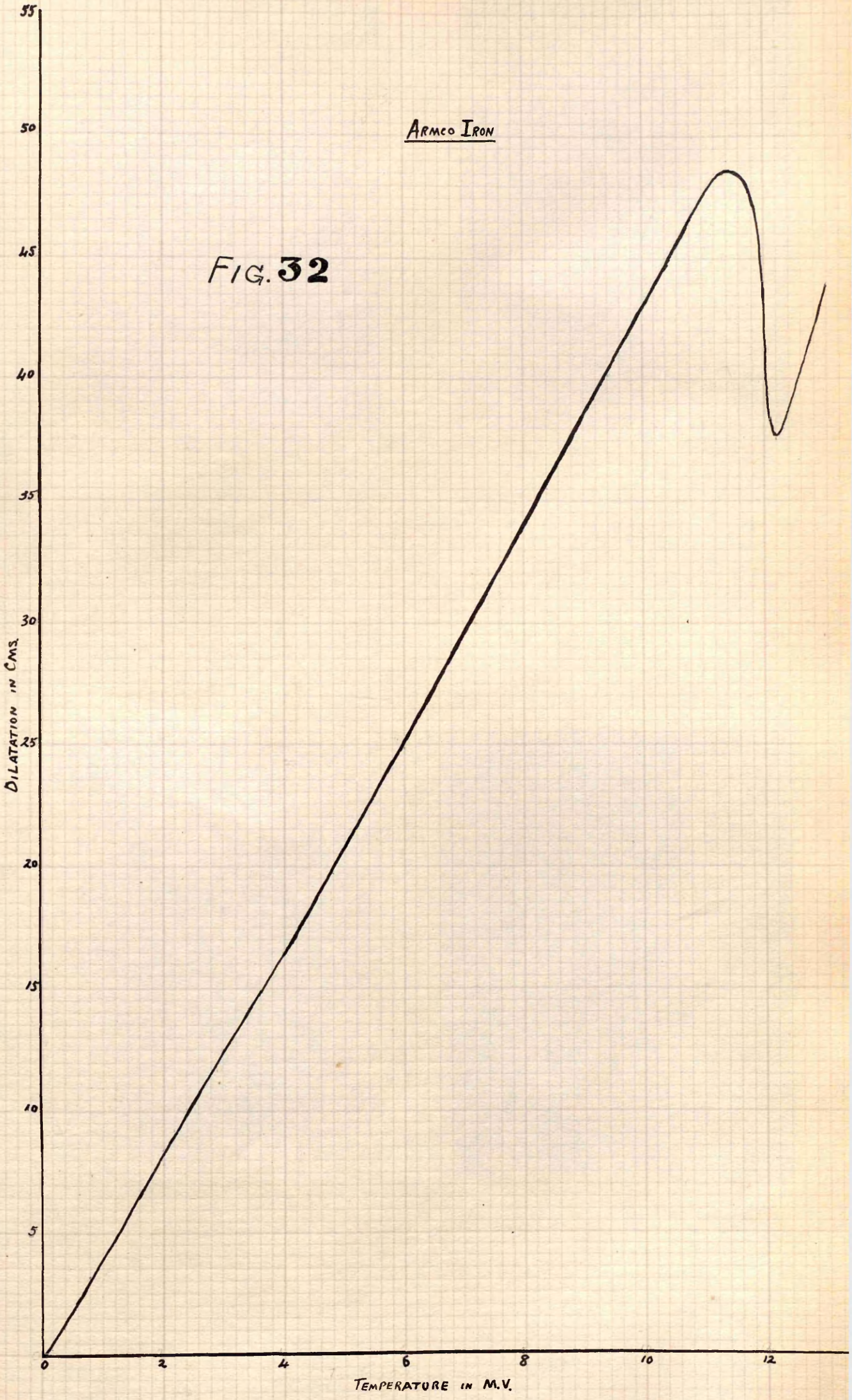

ARMCO IRON
55
50
45
40
35
30
25
20
15
10
5
DILATATION IN CMS.
0
2
4
6
8
10
12
TEMPERATURE IN M.V.

Fig. 33 β treated with alternating current X600

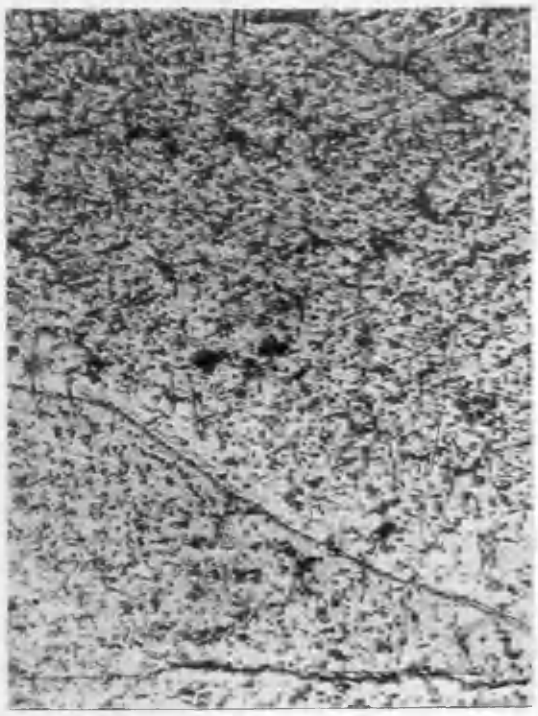


Fig 34. β treated at 330°C X150

Fig 35 alloy as shown in Fig 34 but heated to 700°C and slowly cooled X150

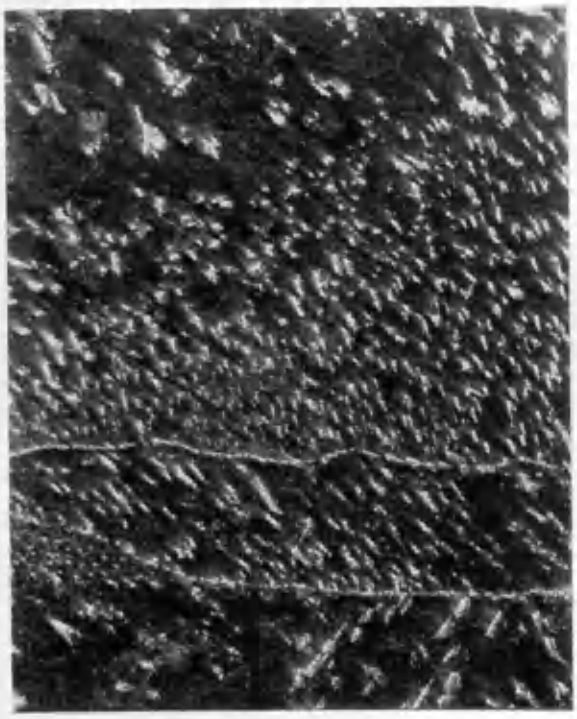
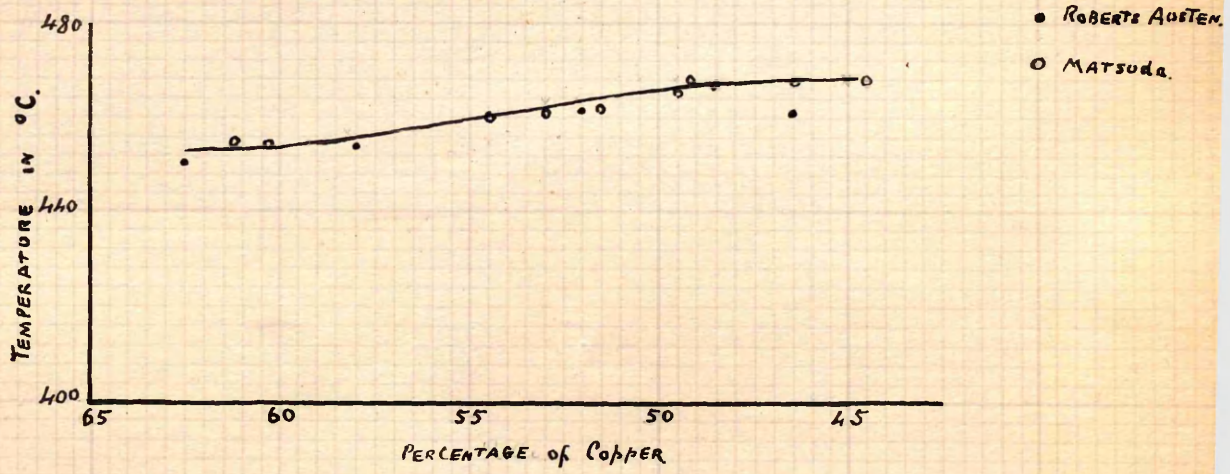


Fig 36. β treated at 330°C for 2 days X150

FIG. 37


480
440
400
TEMPERATURE IN °C.
65
60
55
50
45
PERCENTAGE of Copper
• ROBERTS AUSTEN.
O MATSUDA.

PART 2.

Aluminium alloys containing small quantities of copper up to about 4% and also small quantities of magnesium, usually about one half per cent, have been the subject of much research work in recent years and also the cause of much theoretical speculation. The reason for this state of affairs is that these alloys, known by the name of Duralumin, have become alloys of considerable practical importance. Moreover they possess the peculiarity of greatly improving in their mechanical properties with time, a phenomenon now designated as "age-hardening."

As a result of a long series of brilliant researches by Gayler[1,2] at the National Physical Laboratory, it is now definitely established that the solubility of the compound $CuAl_2$ varies greatly with temperature, being much more soluble at higher temperatures than at room temperature, and that this change in solubility is bound up with the increase in mechanical properties on ageing. Moreover she has shown that the compound $Mg_2Si$ also plays an important part in the age-hardening of these alloys, functioning in a manner similar to $CuAl_2$.

Whilst it has been shown that age-hardening is a direct function of the $Mg_2Si$ content of duralumin, the hardness and other properties increasing with the amount of this substance up to about 1% and also that the $CuAl_2$ functions in a similar manner, though probably not so effectively, yet the physical explanation of the increased hardness is not understood. Certainly it is agreed that the particles must be small which separate although exact physical data showing that these have actually separated is lacking. Admittedly, except by assuming separation, it is difficult to account for the gradual but steady increase of hardness with time

of/

of the original quenched alloy.

Arising from the work already carried out on the transformation in Beta Brasses it appeared very highly probable that the mechanism of age-hardening of duralumin alloys was of the same type, namely, that the hardening was brought about by the deposition from solution of the $Mg_2Si$ and $CuAl_2$ in a state of critical dispersion or, in other words, in the colloidal form. It was realised that microscopical evidence would not be so convincing in this case, as in that of the Cu-Zn alloys, so that recourse was had to a survey of a number of physical determinations, in the hope that they might shed some light upon the problem.

By the way of a preliminary survey a number of heating and cooling curves of duralumin were carried out on differently treated specimens. At this early stage it should be mentioned that all specimens were cut from the same rod of duralumin, a 6 fpot length of 1" diameter, commercial material being used. The temperature was measured by a previously standardised Platinum Platinum-Iridium thermo-couple and a Tinsley Vernier Potentiometer. Great care was exercised in the experimental determinations so that any evidence of the type of change should not be overlooked.

Figure I shows the curve obtained for an annealed piece of the duralumin. The heating curve is practically smooth, there being no sign of sudden solution of the separated phase. That a portion of it has actually gone into solution is evidenced by the cooling curve on which an evolution of heat is marked at 350°C. For the cooling curve determination the current was switched off when a temperature of 520°C was attained, there being no period of soaking at the maximum temperature.

Figure 2 depicts the cooling curve for the same alloy as before but this time it was soaked for a longer period at the/

the high temperature. On this occasion the change point is much larger indicating a larger deposition of the compound. Moreover the temperature of maximum deposition is somewhat higher than before, occurring at 365°C. Whether this point represents only the position of maximum deposition, the intermetallic compound being deposited continuously in small amount over a range of temperature, or whether it is all deposited at this point, is not indicated. Another specimen was heated to 520°C, soaked at this temperature for half an hour, and then quenched in water. The thermal curve was taken immediately after cooling. The heating curve (see Figure 3) shows a small break at 180°C and a much more pronounced break at 280°C. This curve is in very good agreement with the curve of Gayler (2) for a similarly treated alloy. Further it is worthy of note that at 350°C there is a sudden change in direction, this indicating an absorption of heat, as against the marked evolution of heat at 280°C. At 480°C there is another very marked change in the direction of the curve. Here it is suggested that the remainder of the compound goes into solution while the uniform rise in the curve from 480°C to 515°C appears to be due to the uniform rate of heating in the solid solution range. The specimen was soaked for a short time at 510°C and then cooled very slowly in the furnace with the heating current on. At 430°C the current was cut off and the specimen cooled in the furnace, readings of time and temperature being recorded. In this case only a very slight break occurs in the curve at 330°C thus showing that practically all the compound has been precipitated whilst cooling slowly in the furnace.

The annealed specimen from the previous experiment was heated to 350°C and soaked at this temperature for 30 minutes and then the cooling curve was taken. The cooling curve is quite smooth as is shown in Figure 4. This indicates that/

that no solubility occurred up to 350°C. This specimen was also heated to 350°C and immediately cooled in the furnace. This curve was a smooth one showing no break due to deposition of compound. It is therefore concluded that below 350°C there is no solubility of the compound in aluminium.

From the evidence of the thermal curves it appears that the compound goes into solution over a range of temperature, going slowly into solution between 350°C and 480°C, and at the latter figure all the remaining amount of compound goes into solution. Even at this higher figure an appreciable amount of time is required to get all the compound into solution.

How the compound will come out of solution depends very largely upon the rate of cooling. If the alloy be very slowly cooled then the compound separates out at a high temperature. But if the rate of cooling be moderately rapid then a large evolution of heat will occur at about 375°C. The exact temperature at which a maximum effect is observed, varies according to different treatments of the alloys, from 330°C to 375°C.. It would appear that the position of the point varies with the amount of the compounds in solution, which in turn is a function of the initial temperature and period of soaking. If the alloy be heated to 510°C and then immediately cooled in the furnace, time does not permit of all the compound going into solution and the point is found at 360°C. If the alloy is soaked for half an hour at 510°C and then cooled at same rate as before the deposition occurs at 375°C whilst if the alloy, after soaking at the high temperature, is very slowly cooled, then the point occurs at 330°C and is very small. Hence the variation of the thermal point on cooling would appear to be a function of the solubility of the compound in/

in aluminium with temperature and time; the lower the temperature the less the solubility of the compound in aluminium. Consequently the less the amount of the compound in solution the lower will be the temperature reached before the concentration of the compound attains the critical amount which produces precipitation.

If the alloy be quenched so as to retain the compound in solution then, on heating the specimen, the compound is deposited over a range of temperature from 260°C to 295°C with the maximum rate of deposition at 280°C.. There is evidence of a very little deposition at 180°C but as the evolution of heat is very great at 280°C very little of the compound can have been precipitated at the former temperature. At 480°C the compound is re-dissolved but requires a certain amount of time to go completely into solution.

Dilatation Experiments.

A study of the precipitation of the compound was made by means of determining the coefficient of expansion with temperature variation. The apparatus was the same as was used in the study of the Copper-Zinc alloys.

A standard dilatation specimen, 2 inches long by 7/8 inch in diameter, was prepared from a piece of the stock duralumin rod.

The specimen was annealed and then the heating dilatation curve determined. This is shown in Figure 5. It will be observed that the curve is a straight line upon to the temperature of the solution of the compound at about 500°C.. Moreover the compound goes into solution causing an expansion of the alloy. There is no evidence in this case of the compound going slowly into solution at lower temperature.

The specimen was heated to 560°C, soaked for half an hour, and then quenched in water. The dilatation curve was taken immediately after quenching. Figure 6 shows the results obtained/

obtained. The coefficient of expansion is quite uniform up to 240°C, indicating that up to this point there has been no change in the material. At 240°C the specimen commences to expand at an increasing rate and the rate of expansion reaches a maximum at 280°C.. From 280°C to 350°C the rate of expansion is about the same as for the solid solution, that is for the range below 240°C.. At 350oC the slope of the curve again changes but this time the rate of expansion becomes less, this being due to the gradual coalescing of the particles of the separated compound. It has already been shown that the compound goes into solution with an expansion. At 430°C of the heating current was cut off and the cooling curve taken. The curve shows a change in direction at 240°C contracting at a lesser rate below this temperature than above it. It would appear that over the range of temperature from 430°C to 240°C the small amount of the compound which must have gone into solution on heating, or had not been deposited, was gradually being precipitated. This is in agreement with the thermal curves. However there exists the apparent anomaly of the compound being deposited on heating with expansion and being deposited on cooling with contraction. Moreover it would appear that the coefficient of expansion for the solid solution and for the aluminium with the compound out of solution is very nearly the same, the latter being just a little less than the former. This is due, in all probability, to the coalescing of the very finely divided particles of the compound which separate from the quenched solid solution upon heating. This view is supported by the evidence of Figure 7.

Another specimen from the same bar was soaked at 500°C for 15 minutes and then quenched in water. The dilatation curve for the quenched specimen was determined and is shown in Figure7. The curve shows the same type of expansion over the range of

temperature/

temperature from 240°C to 280°C but because of the shorter time of soaking the amount of expansion is not quite so great. Beyond 280°C the curve shows that a gradual coalescing of the particles took place, indicated,, as before, by the gradual decrease in the rate of expansion. At 430°C the decrease in the rate of expansion becomes much more pronounced, but at 480°C the rate of expansion increases, due to the solution of the compound. At 510°C the heating current of the furnace was cut off. From this temperature down to 430°C the curve shows an increasing rate of contraction due to the continuous precipitation of the compound. From 430°C to 180°C the rate of contraction is constant. Upon reheating the specimen the rate of expansion is exactly the same as was the rate of contraction on cooling. The curve continues as a straight line up to 480°C at which temperature the rate of expansion increases. This indicates that once the compound has come out in the massive form it does not go into solution again until 480°C. It is worthy of mention that the annealing of the quenched specimen had caused it to undergo a net contraction. Figure 8 shows the derived dilatation curve. The close resemblance to the derived thermal curve for the quenched alloy is most striking.

In Figure 9 is shown the dilatation curve of a specimen which had been quenched from 500°C and then aged for 24 hours at room temperature. Comparing Figs. 6 and 9 the same thermocouple was used in these two cases - it is noticeable that the rate of expansion is greater in Fig.6.. Moreover there is little evidence of precipitation in Figure 9, indicating that practically all of the compound has separated in the 24 hours. Further the cooling curve practically follows the heating curve, there being no difference in the/

the final readings. This also points to the fact that all the compound had separated during the 24 hours of ageing. The cooling curve shows a slight decrease in the rate of contraction at 240°C from which it would appear that there had been a small amount of the compound going into solution although the maximum temperature was below 480°C.

Another specimen was soaked for 3 hours at 500°C and then quenched in a mixture of ice and brine. Figure 10 shows the heating dilatation curve obtained using this specimen. The same expansion and gradual contraction due to the precipitation and coalescence of the compound is revealed. Also the expansion at 480°C due to the precipitated compound redissolving, is observed.

From the evidence supplied by a study of the dilatation curves, it appears that the compound separated from the solid solution causing an increase in volume. This precipitation took place at about 280°C.. This was followed by a gradual contraction, due to the coalescence of the finely dispersed precipitate, which finally went into solution again at 480°C. It was further demonstrated that a small amount of this finely divided precipitate went into solution below 480°C but if the precipitate became coalesced, or massive, it did not go into solution until 480oC. This influence of the state of subdivision upon solubility is quite general throughout the realm of chemistry.

Thermo-electric Power.

The thermo-electric power of variously treated duralumin specimens was determined in order to see if a study of this physical property would throw any light upon the "age-hardening" of these alloys. For this purpose the thermo-electric value against platinum was determined. The duralumin specimens were in the form of thin strip about $\frac{1}{4}$ inch thick and of the same breadth. Each strip was 6 inches long.

A/

A small electric resistance furnace was made out of a fire-clay sheet and platinum wire. The total length of the furnace was ½ inch. The furnace was placed upon the junction of the piece of duralumin strip and the platinum wire in the form of a cap, the other end of the strip being immersed in cold water. The strip did not make contact with the water but was enclosed in a glass tube. The platinum limb of the couple was similarly cooled. The cooling of the cold junctions was sufficiently drastic to prevent the "aged" alloy from becoming soft and also to prevent the quenched alloy from "ageing". The thermo-couple for recording the temperature was of platinum, platinum-iridium, a Tinsley potentiometer being used to measure the current. The same potentiometer was used to determine the thermo-electric power. The hot junction of the thermo-couple was enclosed in a sheath but in view of any possible lag in the temperature this was discarded. It was next tried without a sheath but the danger of "shorting" was ever present. Finally it was separated from the thermo-pile by a piece of fireclay sheath which had been split in two. This prevented "shorting" and did not give rise to any possibility of a lag in the temperature recorded. That the apparatus was capable of giving good results can be seen from Figure 11, in which is shown the curves obtained from two strips of annealed duralumin. An interval of three months elapsed between the determination of the two curves.

The thermo-electric values of the strips of duralumin in the annealed, quenched, and age-hardened states against the same piece of annealed platinum wire were measured at various temperatures from room temperature to 450°C. The thermo-electric value was determined at intervals of 10 micro-volts in the thermo-couple circuit, which was equal/

equal to approximately 10°C.. The results of these determinations are seen in Figure 12 in graphical form.

The curve for the annealed specimen calls for no comment being smooth and similar to those of Figure 11. Both the aged and the quenched states gave higher thermo-electric values than the annealed state. Consequently both curves lie above that for the annealed specimen and, moreover, not even at high temperatures do they approach it. On the other hand above 280°C the curves for the quenched and the aged specimens coincide. It would appear, therefore, that the state of the compound which separated from the quenched solid solution upon heating is not the same as that which separated upon slowly cooling. Although this contention is supported by the evidence obtained from the dilatation curves, yet it must be noted that in the case of the treated theremo-electric specimens whilst the hot end of the specimens underwent change, the cold end remained in the treated state. This, undoubtedly, would account for a portion, if not all, of the difference between the curves. One of the treated specimens was heated to 500°C and slowly cooled and gave the characteristic curve for the annealed state. It will also be observed in Figure 12 that at low temperatures, the quenched state gave higher thermo-electric values than the aged state but that the rate of increase of the thermo-electric force for the quenched state began to fall away about 120°C.. At 170°C the curve for the quenched specimen falls below that of the aged specimen and continues to remain below until 260°C at which temperature it rises again and at 280°C the two curves very nearly merge together. The quenched state gave the greatest thermo-electric value and the aged state also gave a greater value than the annealed state. When the compound separated from solution in a very fine state/

state of division it caused a lowering of the thermo-electric value, due to the strained state of the alloy, and actually lowered the value below that of the aged curve. This would be expected because the particles which separated during the process of ageing in the aged specimen would pass into a slightly coarser state during the subsequent heating, and the specimen would be less strained, whereas in the quenched alloy the particles ~~which~~ would just be separating from the solid solution on heating. These latter particles also gradually pass into the coarser state with increasing temperature and further deposition takes place until at 280°C the states of the two specimens become practically identical, except for slight differences in cold ends; also complete deposition takes place at this temperature as shown by the thermal and dilatation curves.

In order to be certain that the strained state did actually lower the thermo-electric value below that of the aged state two further experiments were carried out. A piece of duralumin strip was worked by passing it through rolls until it was reduced by 50%. Another piece of strip was quenched from 500°C and aged in boiling water for 20 minutes. The thermo-electric value of each specimen was determined against the annealed platinum wire with increasing temperature. In Figure 13 the results obtained are shown graphically and it is seen that the cold worked specimen gave a lower value than the aged specimen. The two curves do not coincide because the cold ends remained in different states.

Dilatation and thermo-electric determinations having demonstrated that the particles of the compound separate in a very fine state of division and then coalesce with increasing temperature, it seemed very desirable to see if the same thing happened on ageing at room temperature.

The dilatometer suggested itself to be the most likely piece/

piece of apparatus with which to demonstrate this point. Accordingly a dilatation specimen was prepared. It was heated to 500°C, soaked for 15 minutes and quenched. The quenched specimen was put into the dilatometer, great care being exercised in setting up the instrument so as to put only a very slight pressure on the specimen. This was necessary, otherwise the dilatometer would not settle down to equilibrium conditions for nearly an hour. Time - dilatation readings were taken, at first at every half hour, and later at longer intervals of time. The curve was of a peculiar rhythmic form. The experiment was repeated but this time the temperature of the air near the dilatometer was also recorded. The results are plotted in graph form in Figure14. It is seen that the rhythmic form of the curve was due to the diurnal fluctuations in room temperature. But it is worthy of note that the first rise in the curve is greater than the succeeding ones. The experiment was repeated but this time it was commenced in the evening when the room temperature was falling, and readings were taken throughout the night. Here again, whilst the dilatation curve follows the temperature curve, yet at first it shows an appreciable rise whilst the temperature is rapidly falling.

Whilst this evidence cannot be said to be conclusive yet it does point, in a strong manner, to the process of ageing at room temperature being the same as that discussed for increasing temperature.

The dilatometer having failed to show what was wanted in a convincing manner, attention was turned to density determinations. However, instead of making complete density determinations, the object in view would be quite as fully served by observing the change in weight in oil of the quenched specimen. Accordingly a specimen of about 13 grams was prepared. All the surfaces were polished, finishing on the/

the 000 French emery paper. This was done so that a smooth face would be obtained and air bubbles would not readily adhere to it. The specimen was heated in vacuo to 500°C, soaked for 15 minutes and quenched in water. It was lightly rubbed on the 000 paper, then transferred to a fine platinum wire cage suspended from one beam of the balance and immersed in paraffin oil. It was counterbalanced by weights and then at half hour intervals, and later at longer intervals, the balance was adjusted by means of the rider and the alteration in weight recorded. The results are shown in graphical form in Figure 16.

The graph rises sharply for the first five hours and then gradually falls again. This change bears out the evidence of the dilatometer in that the ageing at room temperature is accompanied by an expansion followed by a contraction. However in this curve the influence of the diurnal temperature variation is also marked. The dotted line will represent, approximately, the true variation due to the ageing of the quenched duralumin. The peaks in this curve occurred between 3 and 4 o'clock in the afternoon, those on the dilatation curve occurring at 2-30 p.m.. In this case the oil would gradually alter in temperature and thus cause an apparent alteration in the specific volume of the specimen. The weights would also alter with temperature.

In order to overcome this difficulty another specimen of the same size was prepared. The two specimens were now annealed and had their surfaces cleaned. One was suspended from each arm of the balance by a platinum cage made of the same wire. Each specimen was immersed in a beaker of paraffin oil to the same depth and each beaker had the same quantity of oil in it. The pointer was adjusted to zero position on the scale and then readings

were taken as before. As both specimens were in the same state no change should take place. This was found to be the case as is shown in Figure 17 upper curve.

One of the specimens was now quenched in water from 500°C after soaking at that temperature for 15 minutes. It was then replaced in the balance and, after adjustment of the weights, the alteration in weight with time was determined. In Figure 17 the results are given in the lower curve. This time the curve is quite regular.

Again there is the marked expansion followed by a slow contraction. Therefore it would appear that the phenomenon accompanying the ageing of a specimen at room temperature was the same as was observed with increasing temperature. It is of interest to note that Igareshi (3) has obtained the same type of curve using a differential dilatometer. The next step to be taken was to investigate the nature of the separating particles. It was now known that increase of temperature, and increase of length of time brought about the same effect upon the quenched duralumin, namely they produced a deposition of the compound in a very fine state of division which gradually coalesced into larger particles. In view of the work which had already been carried out upon the brasses of Beta composition it was thought desirable to apply the same treatment to the quenched duralumin. If such treatment hastened the coagulation of the finely deposited particles, then a most feasible assumption to make was that the separating particles were of a colloidal nature.

The method of investigation which most readily suggested itself was to follow the change in constitution of the alloys by means of Brinell Hardness determinations. The work of Hanson, and Gayler (4) has shown that there is a considerable increase in the Brinell Hardness as ageing proceeds. For the purpose of experiment two

pieces/

pieces of the duralumin rod, each about 6 inches long, were machined so as to have their top and bottom faces parallel for the determination of the Brinell Hardness values. Also one piece was turned down to 3/8 of inch diameter at each end for a length of ½ inch. This was for the purpose of fitting terminals to connect to an alternating current circuit. Both specimens were quenched from 500°C in cold water and the Brinell Hardness number immediately determined. The one specimen was then put into the secondary circuit of an induction coil giving about 50,000 volts and submitted to the alternating current at room temperature. No rise in temperature of the specimen occurred. The other specimen lay on the bench near to the specimen under treatment but received no treatment. Brinell Hardness determinations were made at frequent intervals and the results are recorded in Table I. They are also shown graphically in Figure 18.

TABLE I.

| Time in hours. | Untreated specimen 500 Kg. load. | Specimen treated with alternating circuit. 500 Kg load. |
|---|---|---|
| 0 | 70 (as quenched) | 70 (as quenched) |
| 1.0 | 70 | 72 |
| 1.30 | 72 | 72 |
| 3.0 | 77 | 82 |
| 4.0 | 72 | 80 |
| 5.0 | 80 | 86 |
| 6.0 | 80 | 86 |
| 23.0 | 86 | 93 |
| 24.0 | 90 | 93 |
| 25.0 | 90 | 94 |
| 27.0 | 90 | 93 |
| 29.0 | 90 | 93 |
| 47.0 | 93 | 93 |

In the alternating current tests it should be noted that the current was cut off during the night, that is during the interval from 6 hours to 23 hours.

Although the results do show that the alternating current has appreciably affected the rate of deposition - or the rate of ageing - yet they cannot be said to offer any satisfactory proof of the nature of the deposited particles.

If the deposited particles are of a colloidal nature then they must have a different electronic configuration from the ordinary crystalline particles. Whilst it is true that colloidal substances have been shown by X-ray analysis to have a definite space lattice yet in very many cases they are known to carry an electric charge. Even in the case of neutral colloidal particles, these must have a different electronic configuration from the ordinary crystalline particles and it is this particular configuration which keeps the particles from coalescing. But under the influence of heat or of an alternating current they lose this peculiar meta-stabile configuration, then they behave like normal particles and will coalesce into larger aggregates. If the deposited particles in duralumin during ageing are of a colloidal nature then they too will have, as previously stated, a characteristic electronic configuration. Resistivity measurements should reveal if such a state of affairs exists. Consequently a series of resistivity determinations was made upon duralumin specimens in the annealed, aged and quenched states.

For the purpose of experiment a number of thin strips of the duralumin were prepared, similar to those used for the thermo-electric determinations. Nickle-chromium steel knife edges were clamped on to the specimens at a distance of approximately 3½ centimetres apart. In order that the distance/

distance might remain constant - this being of vital importance - the same specimen was used for the annealed, quenched and aged determinations, the knife edges being kept in position throughout. The drop in potential between the knife edges was measured by means of a vernier Tinsley potentiometer. The current was obtained from four Ni-Fe batteries arranged in parallel, each battery having 3 two-volt cells arranged in series. This gave a steady current which, by means of adjustable rheostats, was cut down to about 1.5 amperes. The current was measured before and after each reading, using a standard shunt and the Tinsley potentiometer. At least 6 resistivity readings were made of each specimen in each state of treatment. All results were calculated to a basis of 1.5 amperes of current, but as comparative results only were required these were not converted to microhms per c.c.. The calculated results obtained for the potential difference did not differ by more than $\pm$ 0.0000025 volts in any set of determinations.

The results obtained were as follows:-

| Annealed state. P.D. in volts. | Quenched state. P.D.in volts. | Quenched and aged in boiling water for 10 mins P.D. in volts. |
|---|---|---|
| 0.00061 | 0.00079 | 0.00082 |

The influence of the time of ageing was next investigated. A quenched specimen was aged in boiling water for different lengths of time and its value finally determined after it had been kept at room temperature for 15 hours.

The results of the experiment are as follows:-

| Time of ageing in boiling water. | Potential difference in volts. |
|---|---|
| 0. minutes (as quenched) | 0.00079 |
| 5 minutes | 0.00082 |
| 15 minutes | 0.00082 |
| 25 minutes | 0.00082 |
| After remaining at room temperature for a further period of 15 hours | 0.00079 |

The specimen was then subjected to alternating current for 30 minutes but the P.D. still remained at 0.00079 volts.

Having shown that heating a quenched duralumin specimen for a few minutes at 100°C brought about an increase in the resistivity but that continued soaking at this temperature up to 25 minutes caused no further change, the influence of raising the temperature was tried. The specimen was heated to 250°C for 15 minutes and finally to 350°C for the same time. The latter treatment reduced the P.D.value to that of the fully annealed state. The following results were obtained, the P.D. being given in volts.

| Quenched state. | Annealed at 250°C for ¼ hr. | Annealed at 350°C for ¼ hr. |
|---|---|---|
| 0.000793 | 0.000766 | 0.000610 |

There is thus quite an appreciable difference in the resistivity values for the different states of the duralumin. Moreover the ageing is accompanied by a distinct change of value. The finely precipitated material causes an increase in the resistivity either due to strain or due to the fact that it is deposited in the colloidal state. It seemed very probable that a few experiments using alternating current on quenched specimens and determining the effect of it by resistivity/

resistivity measurements would throw some light upon this point.

Accordingly a specimen was quenched from 500°C after soaking at that temperature for 15 minutes. It was then aged in boiling water for 10 minutes and subjected to the alternating current treatment at the temperature of boiling water. Resistivity determinations were made at each stage of the treatment of the specimen. The following results were obtained. All determinations were made at room temperature.

| Quenched state. | Aged state. | Time in boiling water. | After treatment with alternating current at 100°C for 10 mins |
|---|---|---|---|
| 0.00078 | 0.000795 | 5 mins. | - |
| - | 0.000805 | 10 mins. | - |
| - | - | - | 0.000780 |

Thus the alternating current brought about a reduction of the resistivity value in ten minutes and in a previous experiment after 25 minutes' treatment in boiling water without alternating current there was no reduction in the initial aged value of the resistivity.

As these experiments seemed to add weight to the observation made by the Brinell Hardness tests, that the alternating current does affect the coalescence of the precipitated compound, it seemed very necessary to carry out some additional experiments upon this point.

It was considered very desirable to follow the ageing phenomena by means of resistivity measurements. An apparatus was set up in which the resistivity specimens were kept at a constant temperature and measurements made at frequent intervals. For the purpose of obtaining constant temperature, two/

two large flasks were fitted with reflux condensers and half filled with water which was kept boiling. One specimen was immersed in the boiling water of each flask.. Further, one specimen was coupled to the alternating circuit, this being cut off by means of a switch when determinations were being made. As before, the current was measured on the potentiometer before and after each reading. Altogether six readings of the specimen in each flask were made alternately at each determination, the limits of error being as before, namely 0.0000025 volts.

The value for each specimen was determined in the cold state after quenching from 500°C and gave the same figure of 0.00061 volts. This figure differs from the earlier ones because the knife edges were a little closer together to permit of easy passage into the flask. Both were mounted in the apparatus and the flasks brought to boiling but no alternating treatment was used at this stage. Further, both were aged for 1½ hours, before the alternating current circuit was coupled to the specimens to be treated. Actually 3 hours elapsed from the commencement of the experiment until the alternating current treatment commenced. After the treatment had started, readings were taken at intervals of 10 minutes, then every half hour and finally at longer intervals. The results are shown in graphical form in Figure 19. For the first three hours the two curves coincide; this is what should be obtained as, up to the time marked by point P, the experiments were duplicates. P indicates the time when the alternating current was switched on. From $\overset{\rho_o}{A}B$ the resistivity rises steadily due to the increasing temperature. The portion from B to C represents the ageing of the specimens. CD on the curve of the untreated specimen (upper curve) shows the same decrease as was obtained in all the previous experiments, namely the gradual decrease in resistivity as coalescence/

coalescence took place. The fall in resistivity from E to F is due to the cooling of the apparatus. The final reading was taken after removing the specimen from the flask and it is noted that it was practically the same as the quenched specimen. Thus the blank specimen behaved in the same manner as all the earlier specimens on ageing, rising to a maximum and then falling to practically the original value.

In the case of the specimen treated with alternating current the resistivity curve falls very abruptly to the point H within 40 minutes after the starting of the circuit. The fall KL is due to the cooling of the apparatus. As in the case of the control experiment the final reading was taken after the specimen was removed from the flask. In this case the final value was lower than the value for the original quenched specimen.

The effect of the alternating current treatment has been to cause more complete coagulation of the finely precipitated particles and thus cause the resistivity of the treated specimen to approach more nearly to that of the annealed state.

It has been shown that the compound separates from the solid solution in quenched duralumin over a range of temperature reaching a maximum at about 280°C.. The compound goes into solution again at 480°C but if the compound is in a very fine state of division it goes into solution to a limited extent before this temperature is reached. When the compound separates from the quenched solid solution it does so with expansion and this expansion is followed by a contraction due to the coalescence of the finely dispersed compound. This happens on ageing at room temperature and also takes place as the alloy ages with increasing temperature. The state of the separating particles is greatly influenced by/

alternating current. The function of the alternating current is to alter the electronic configuration of the dispersed particles of the separated compound and so allow them to coalesce to a greater extent than would otherwise be possible. Increasing the temperature functions in the same manner. The particles which separate on ageing are in a particular state of dispersion and have a characteristic electronic configuration; in other words they are in the particular state of matter called the colloidal state.

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## References.

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   Gayler. Journ. Inst. Metals. Vol.XXVIII. 1922.
   Gayler. Journ. Inst. Metals. Vol.XXIX. 1923.
2. Gayler. Journ. Inst. Metals. Vol. XXVIII. 1922. p.235.
3. Igarashi. Sci. Rep. Tohoku. Imp.Univ. 1924. (1) 12.
4. Hanson & Gayler. Journ. Inst. Metals. Vol. XXVI. 1921. p.344.

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Fig. 1.

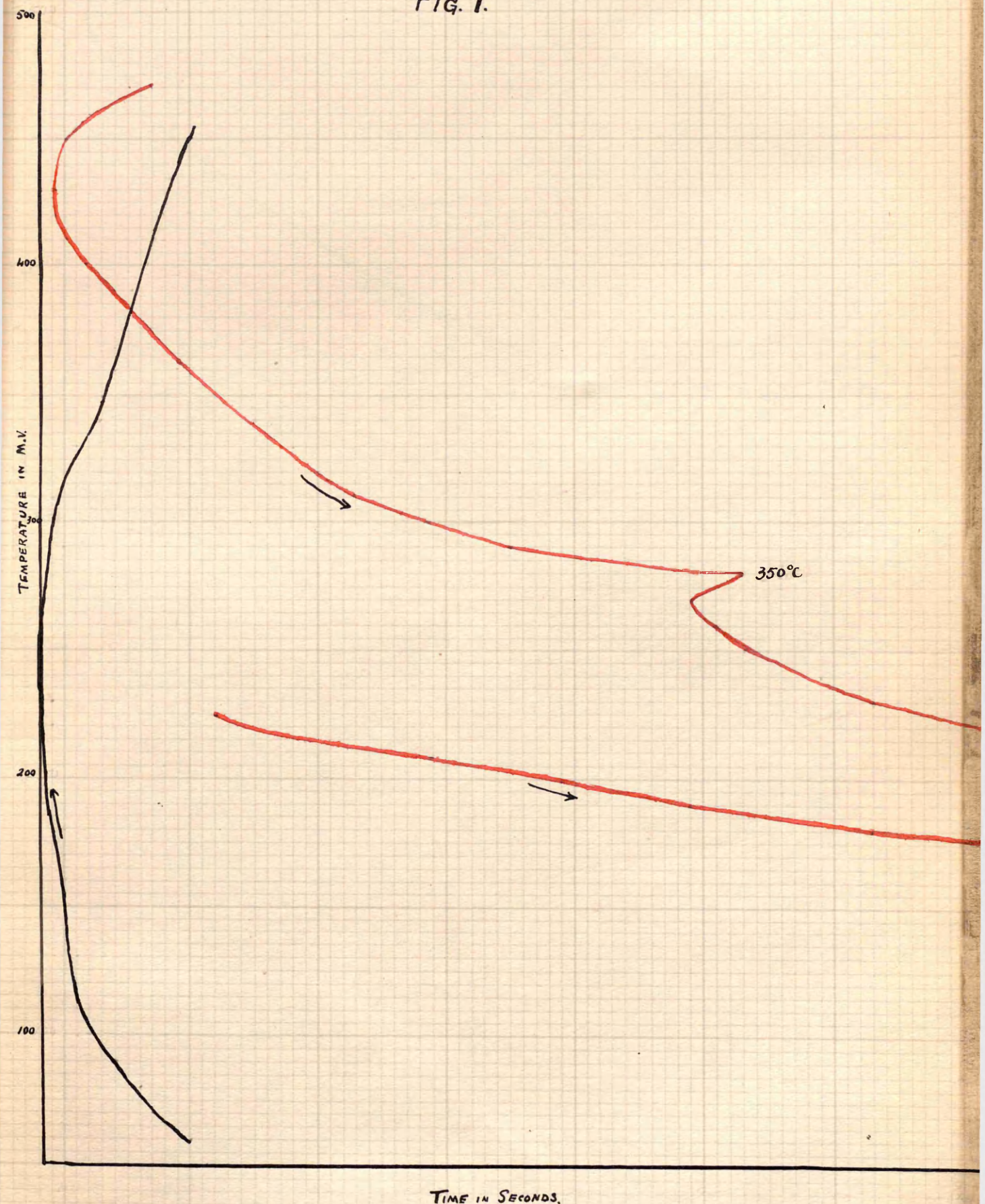


FIG. 2

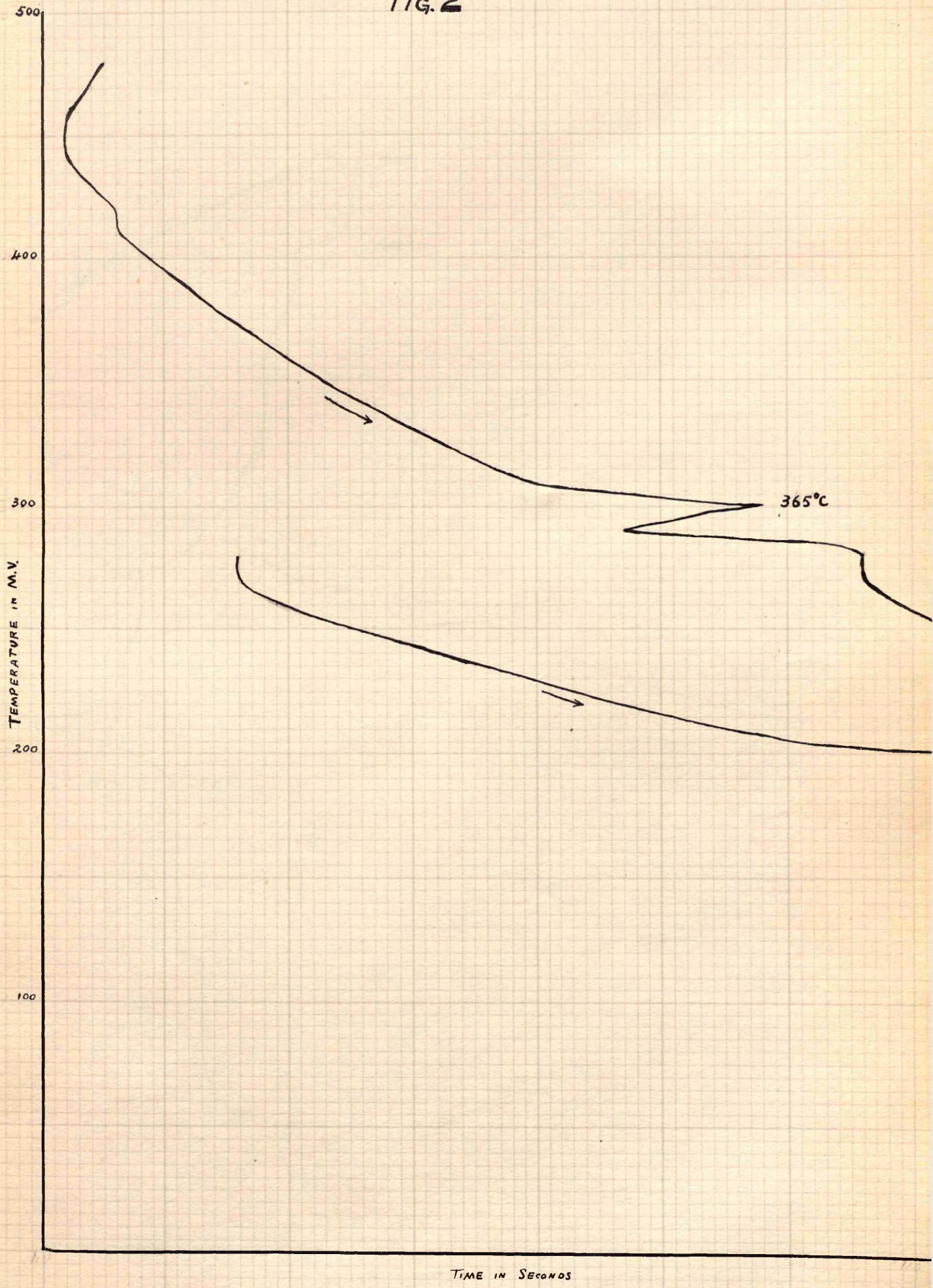


FIG. 3

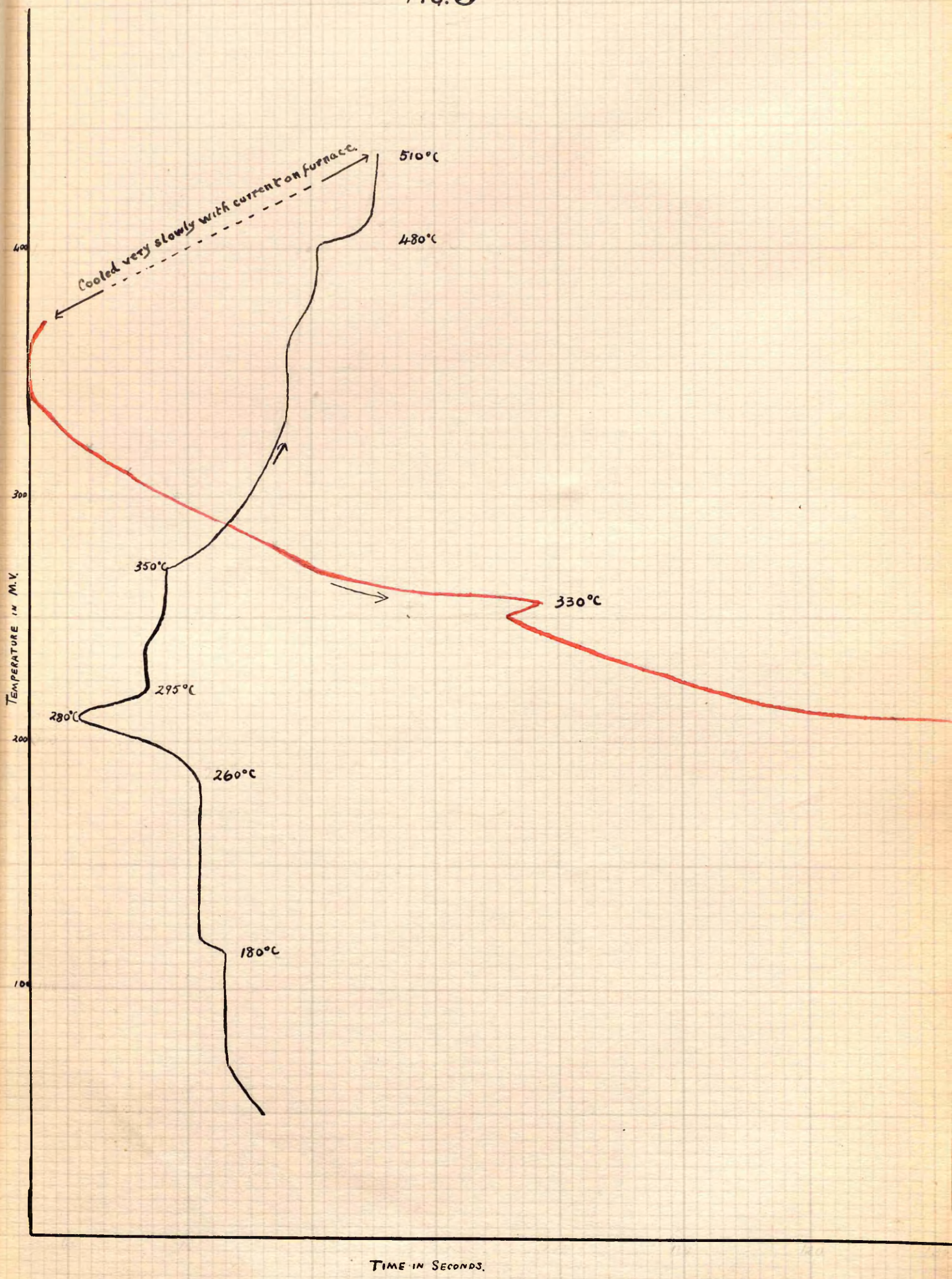
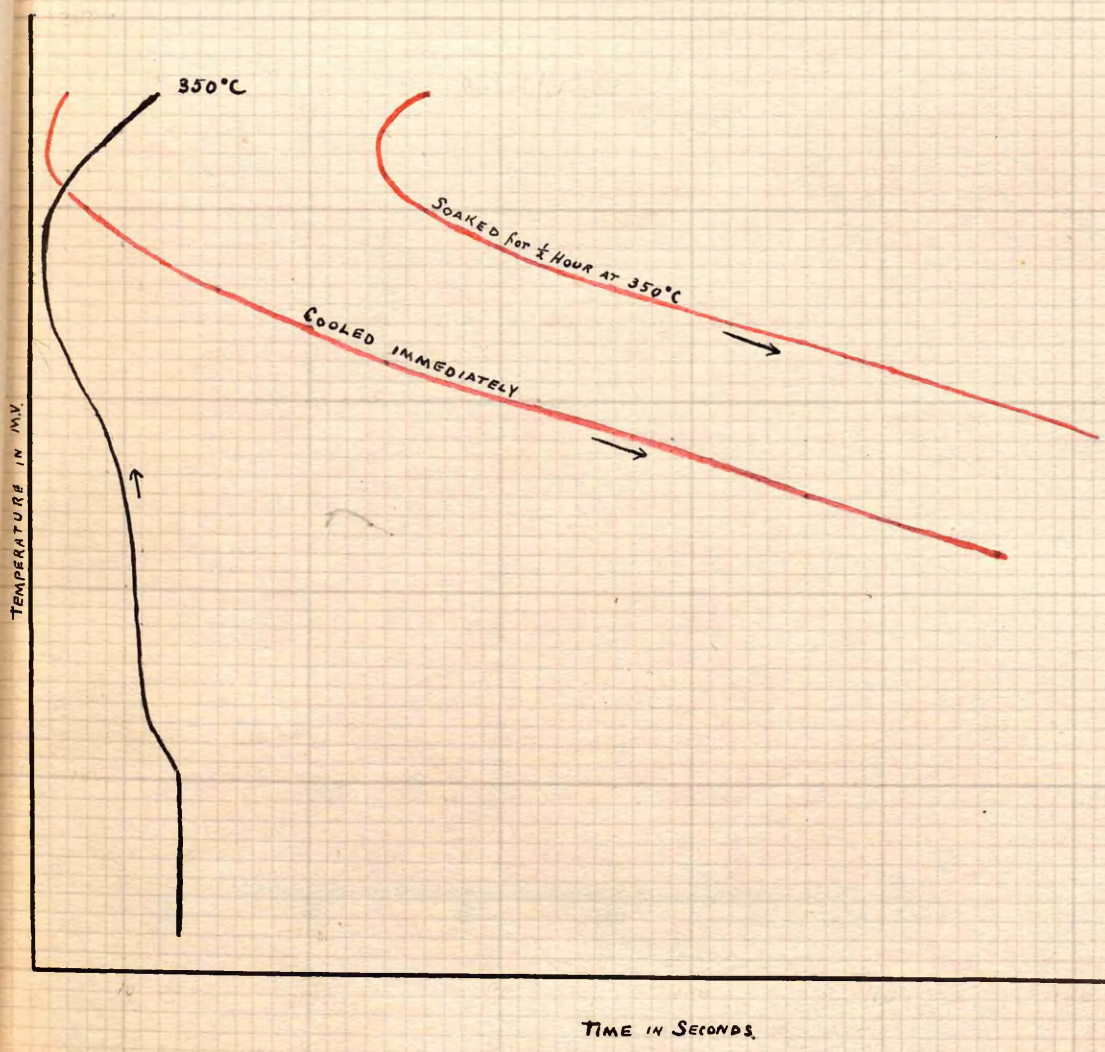

Cooled very slowly with current on furnace.
510°C
480°C
400
300
350°C
330°C
295°C
280°C
200
260°C
180°C
100
TEMPERATURE IN M.V.
TIME IN SECONDS.

Fig 4


350°C
SOAKED for ½ HOUR AT 350°C
COOLED IMMEDIATELY
TEMPERATURE IN M.V.
TIME IN SECONDS

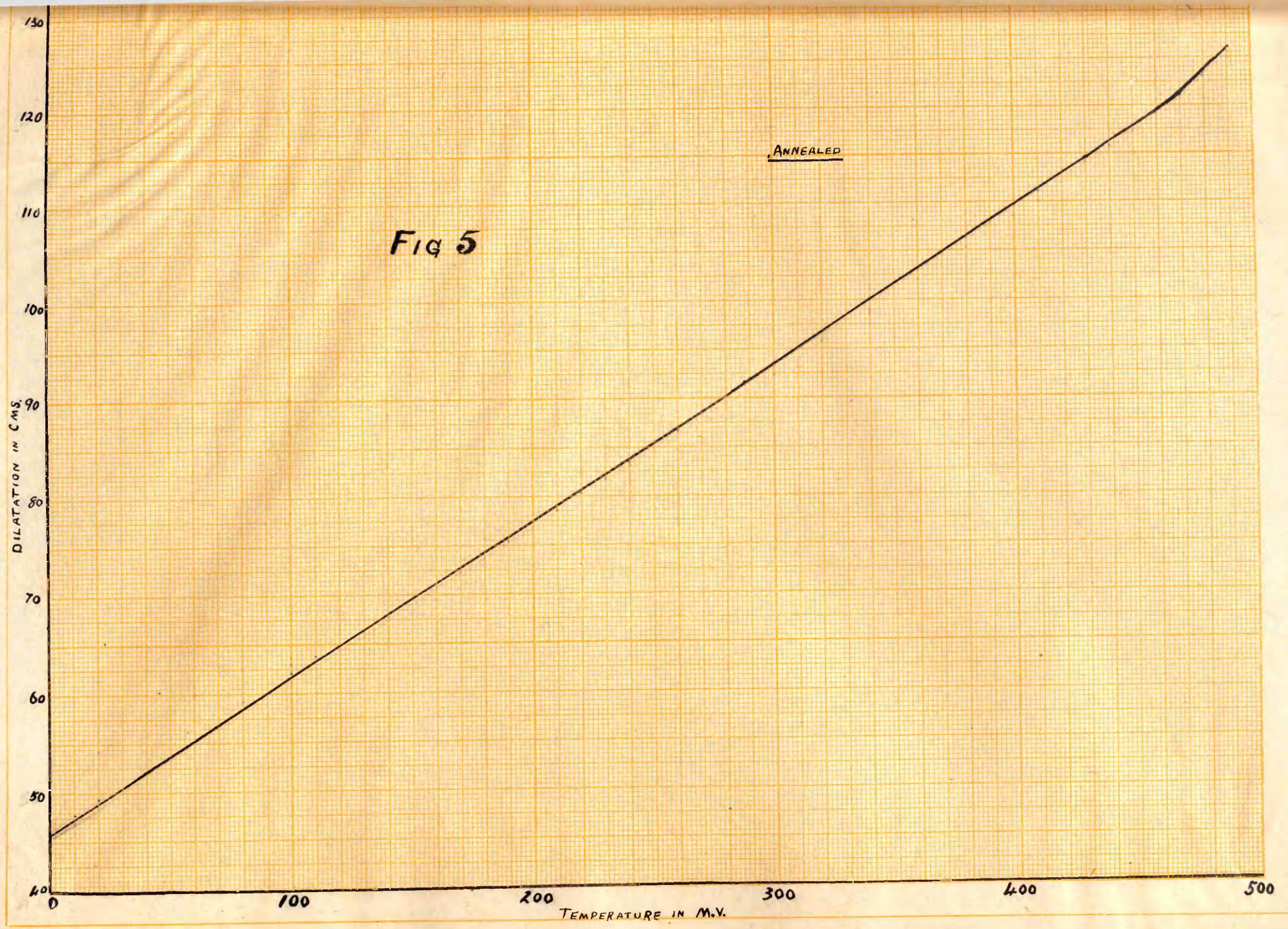

130
120
110
100
90
80
70
60
50
40
DILATATION IN C.MS.
ANNEALED
0
100
200
300
400
500
TEMPERATURE IN M.V.

FIG 5

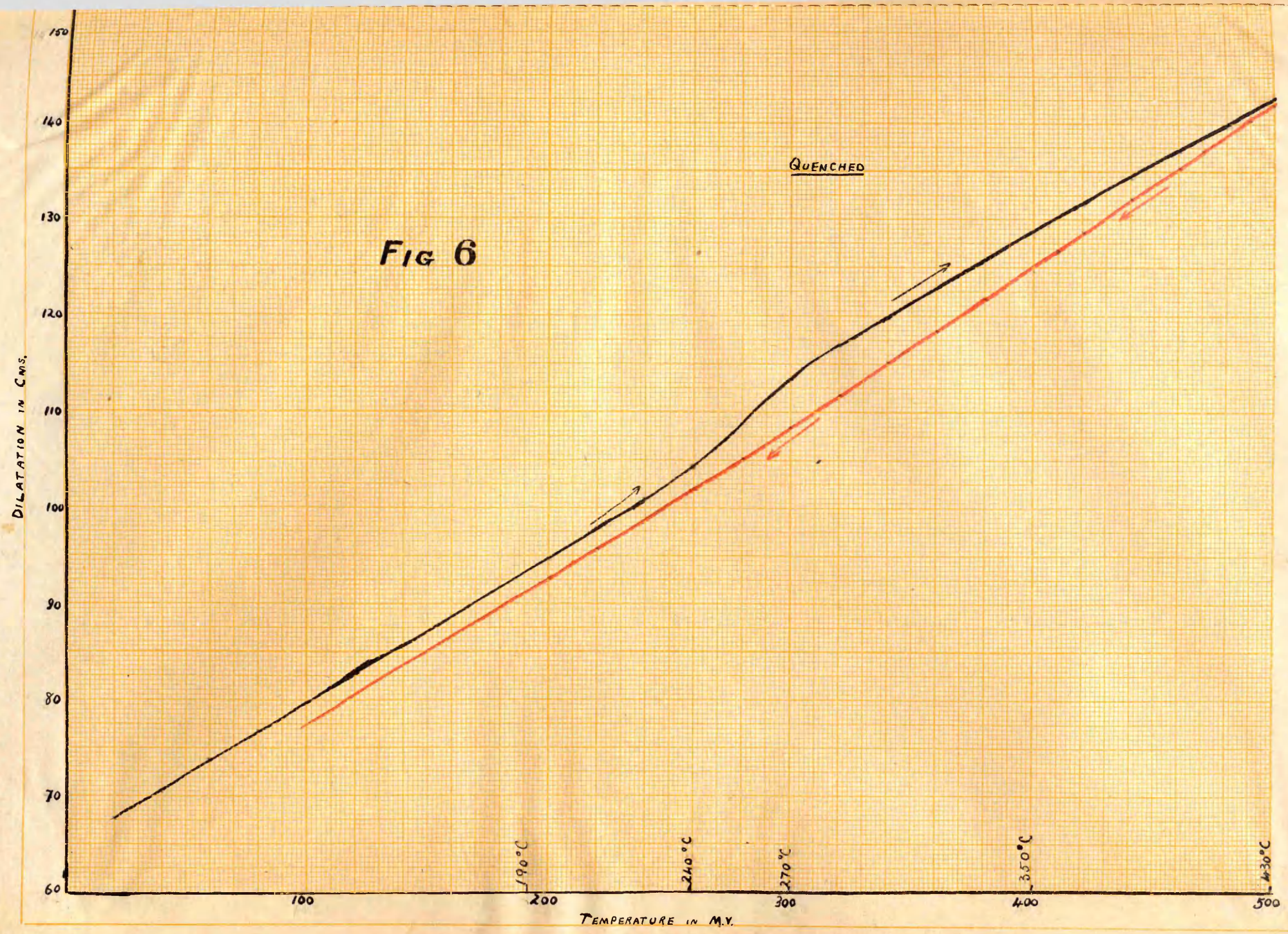


FIG 6
QUENCHED
DILATATION IN CMS.
150
140
130
120
110
100
90
80
70
60
100
200
300
400
500
190°C
240°C
270°C
350°C
430°C
TEMPERATURE IN M.V.

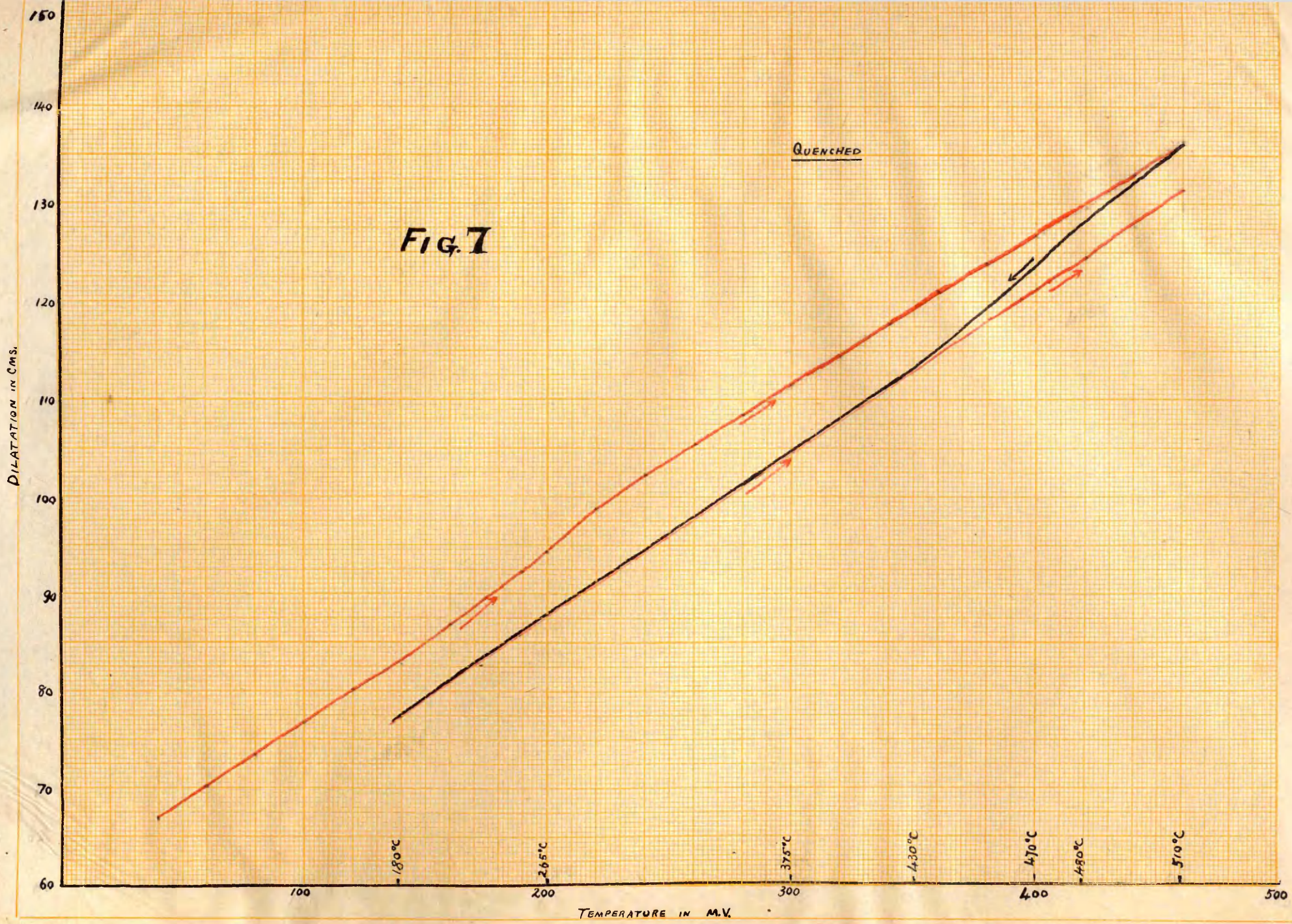
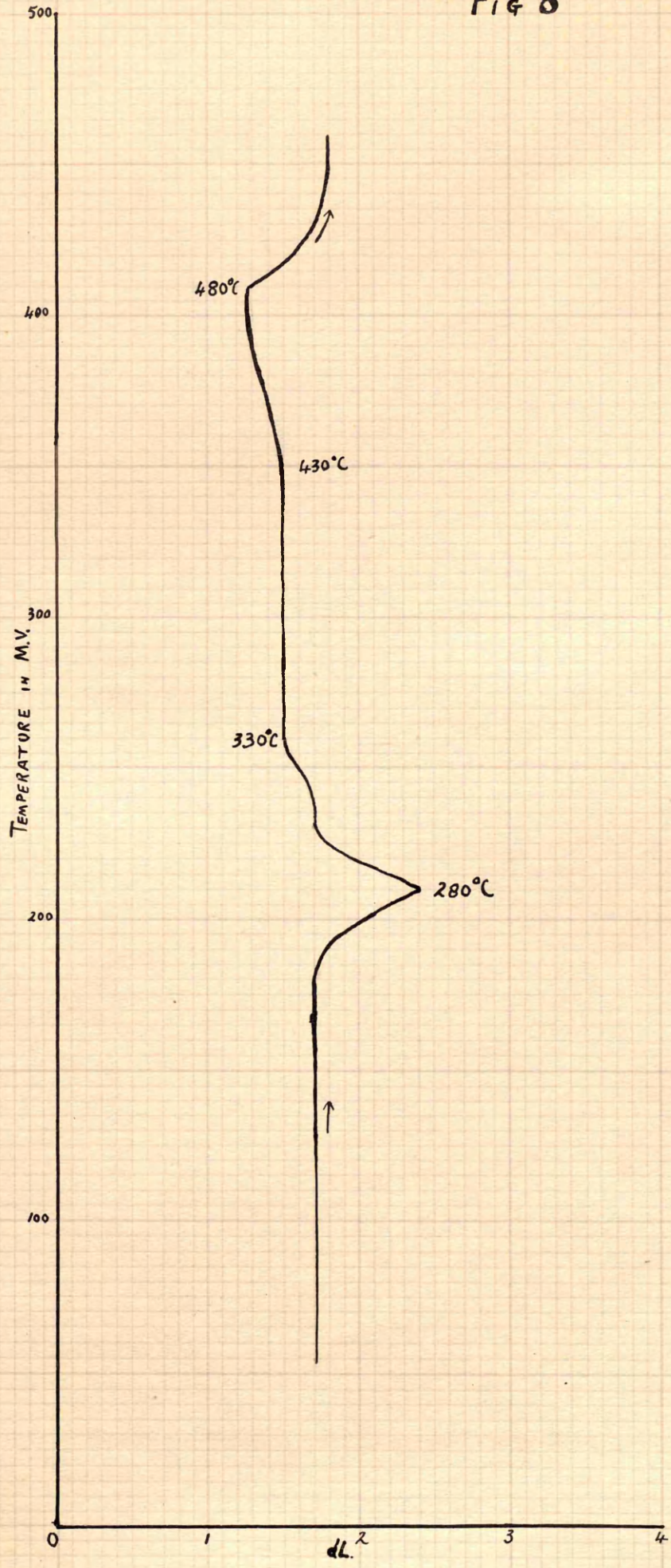
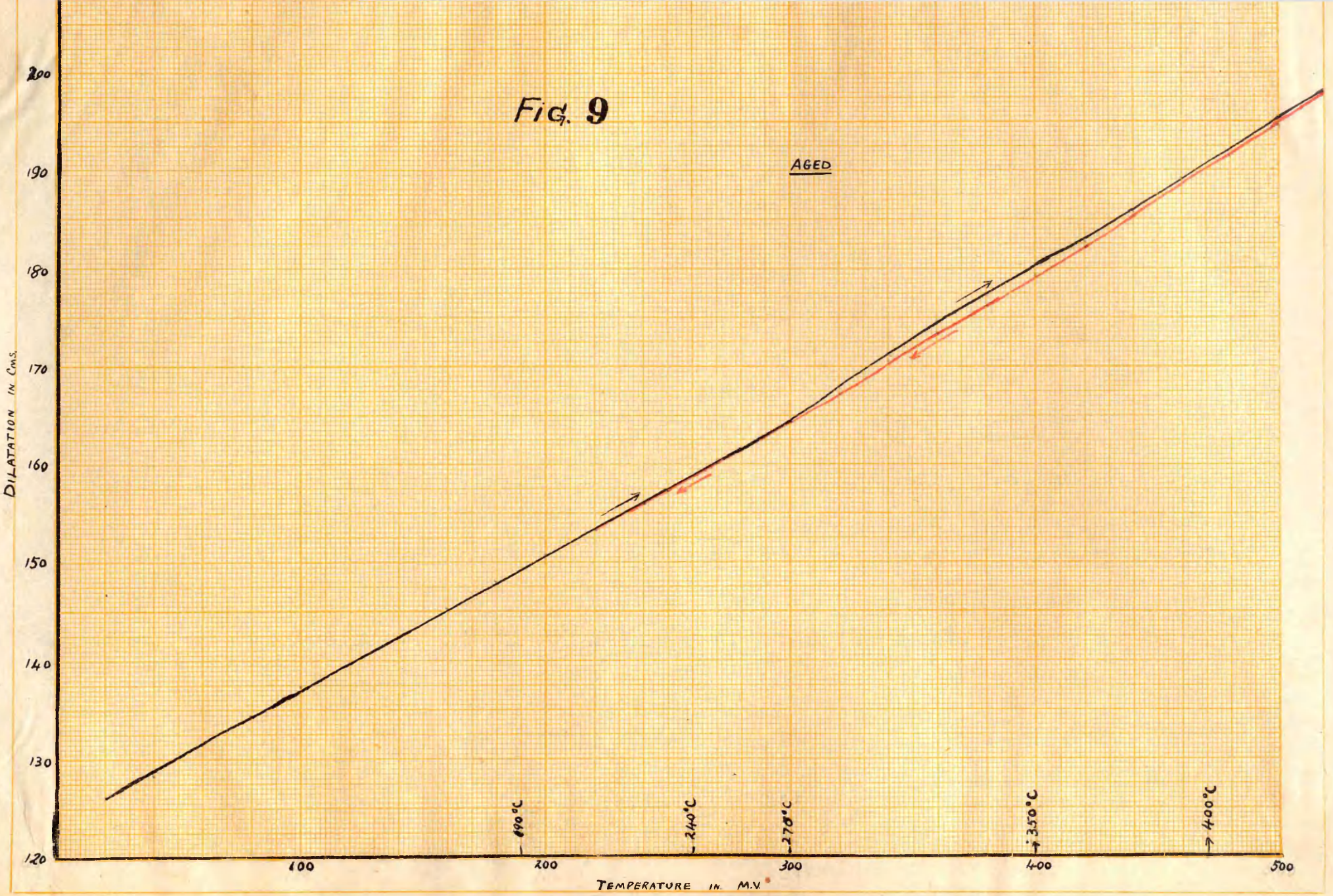


FIG. 7
QUENCHED
DILATATION IN CMS.
150
140
130
120
110
100
90
80
70
60
100
200
300
400
500
180°C
265°C
375°C
430°C
470°C
480°C
510°C
TEMPERATURE IN M.V.

FIG 8


500
400
300
200
100
TEMPERATURE IN M.V.
480°C
430°C
330°C
280°C
0
1
2
3
4
dL.

# Fig. 9


AGED
DILATATION IN Cms.
200
190
180
170
160
150
140
130
120
100
200
300
400
500
190°C
240°C
270°C
350°C
400°C
TEMPERATURE IN M.V.

# FIG 10

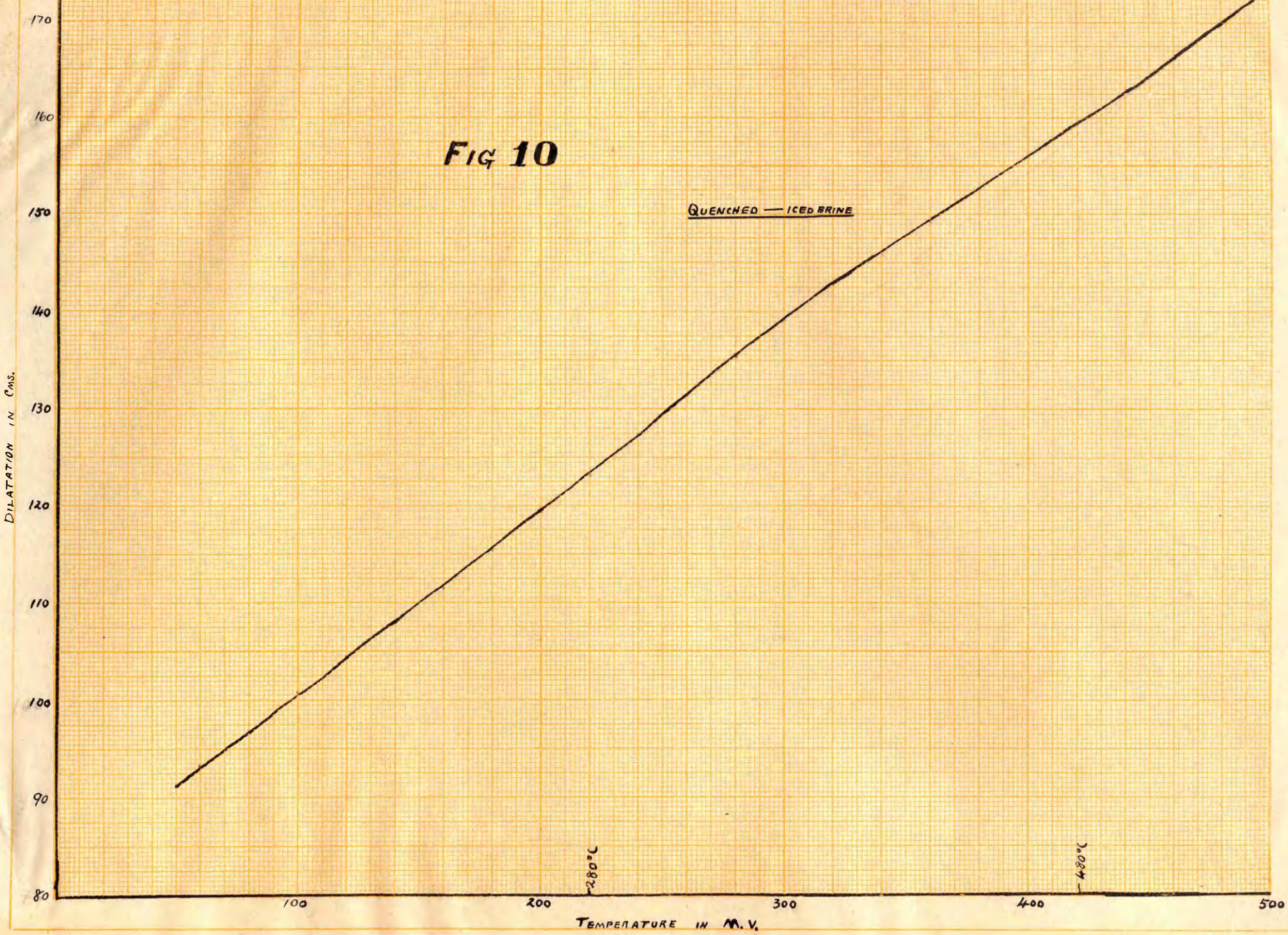
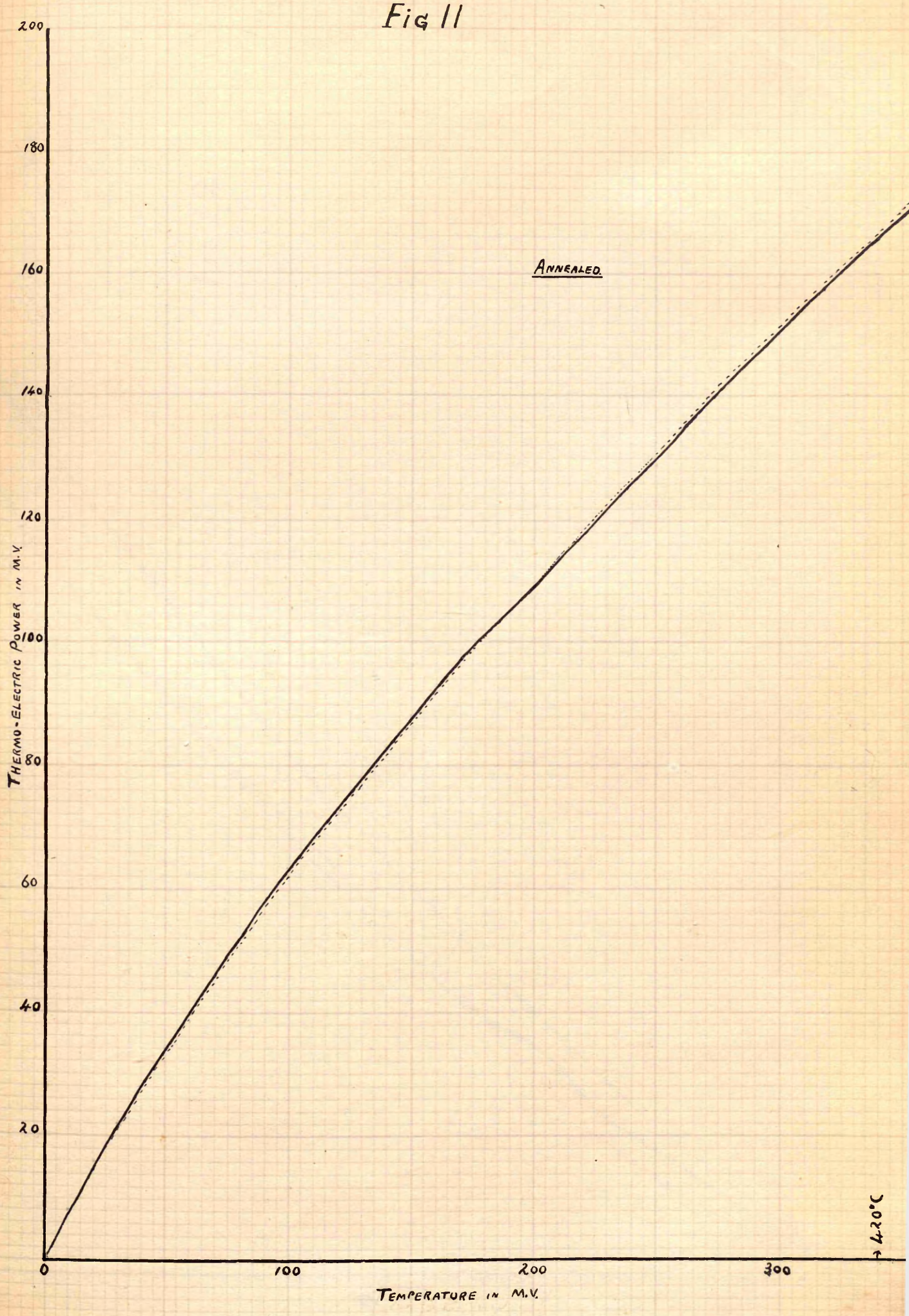

QUENCHED — ICED BRINE
DILATATION IN CMS.
170
160
150
140
130
120
110
100
90
80
100
200
300
400
500
TEMPERATURE IN M.V.
.0082
.0084

Fig 11


200
180
160
140
120
100
80
60
40
20
ANNEALED.
THERMO-ELECTRIC POWER IN M.V.
0
100
200
300
TEMPERATURE IN M.V.
420°C

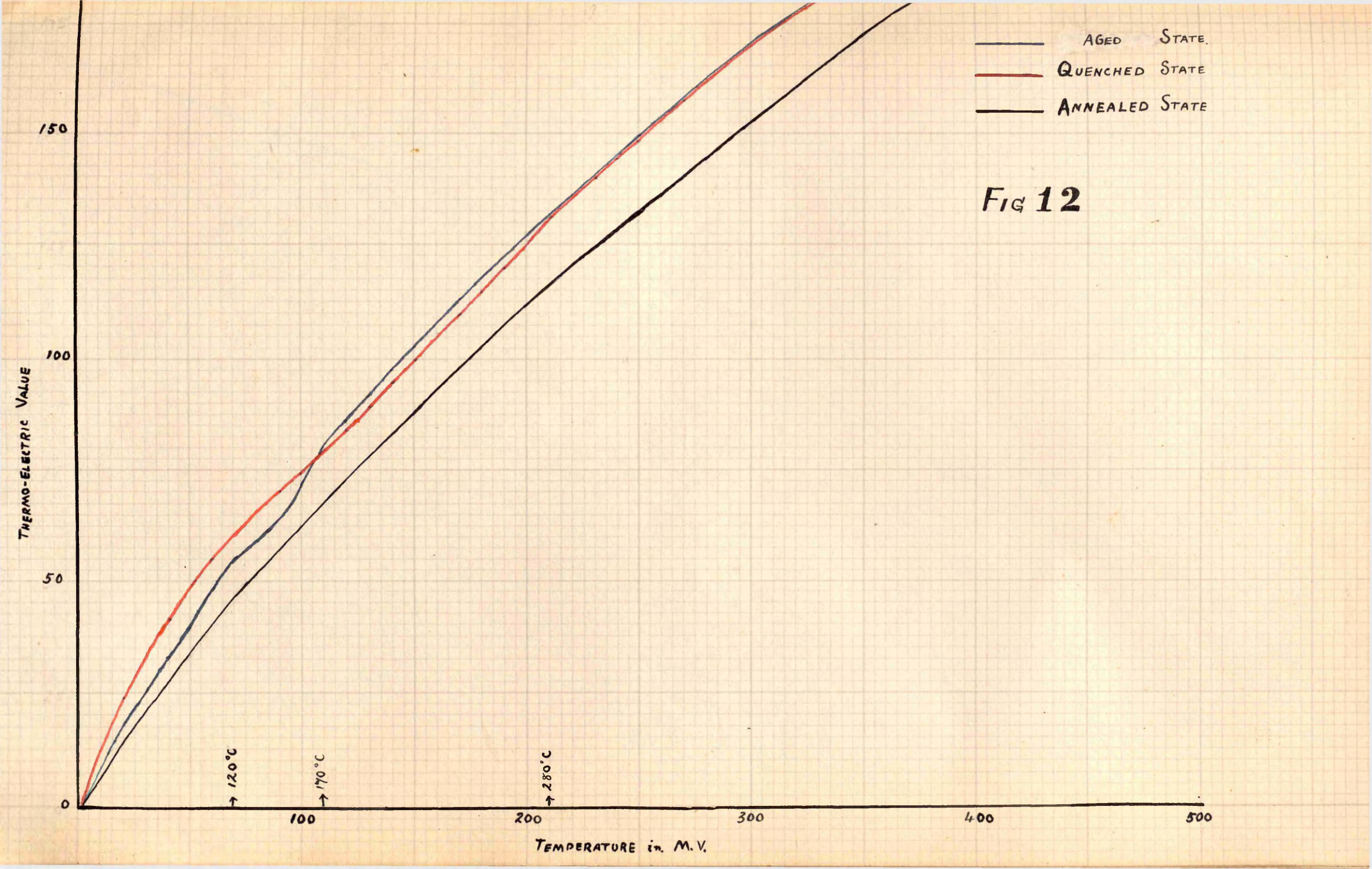

AGED STATE.
QUENCHED STATE
ANNEALED STATE
150
100
50
0
THERMO-ELECTRIC VALUE
120°C
170°C
280°C
100
200
300
400
500
TEMPERATURE in M.V.

FIG 12

FIG. 13

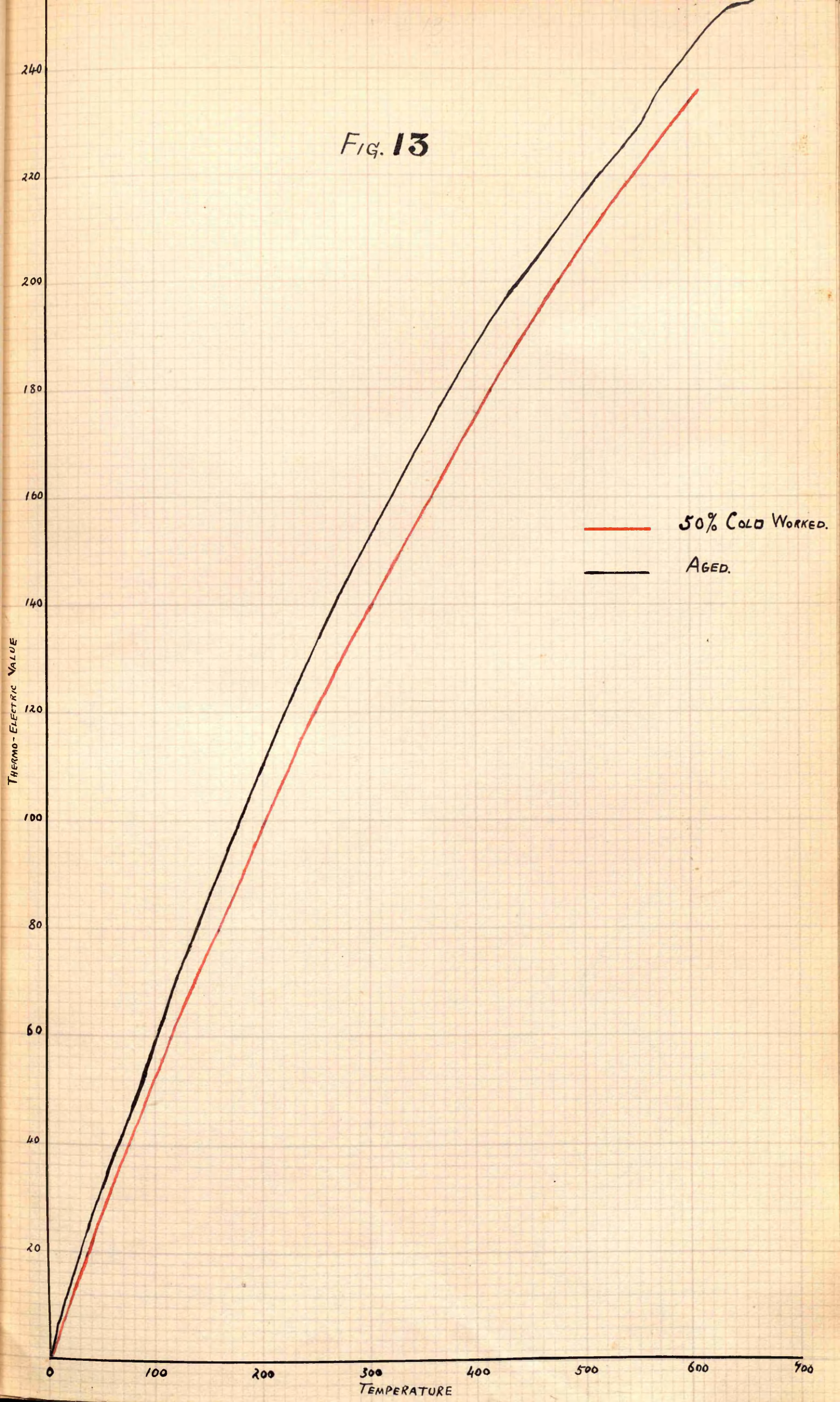

240
220
200
180
160
140
120
100
80
60
40
20
THERMO-ELECTRIC VALUE
0
100
200
300
400
500
600
700
TEMPERATURE
50% COLD WORKED.
AGED.

Fig. 14

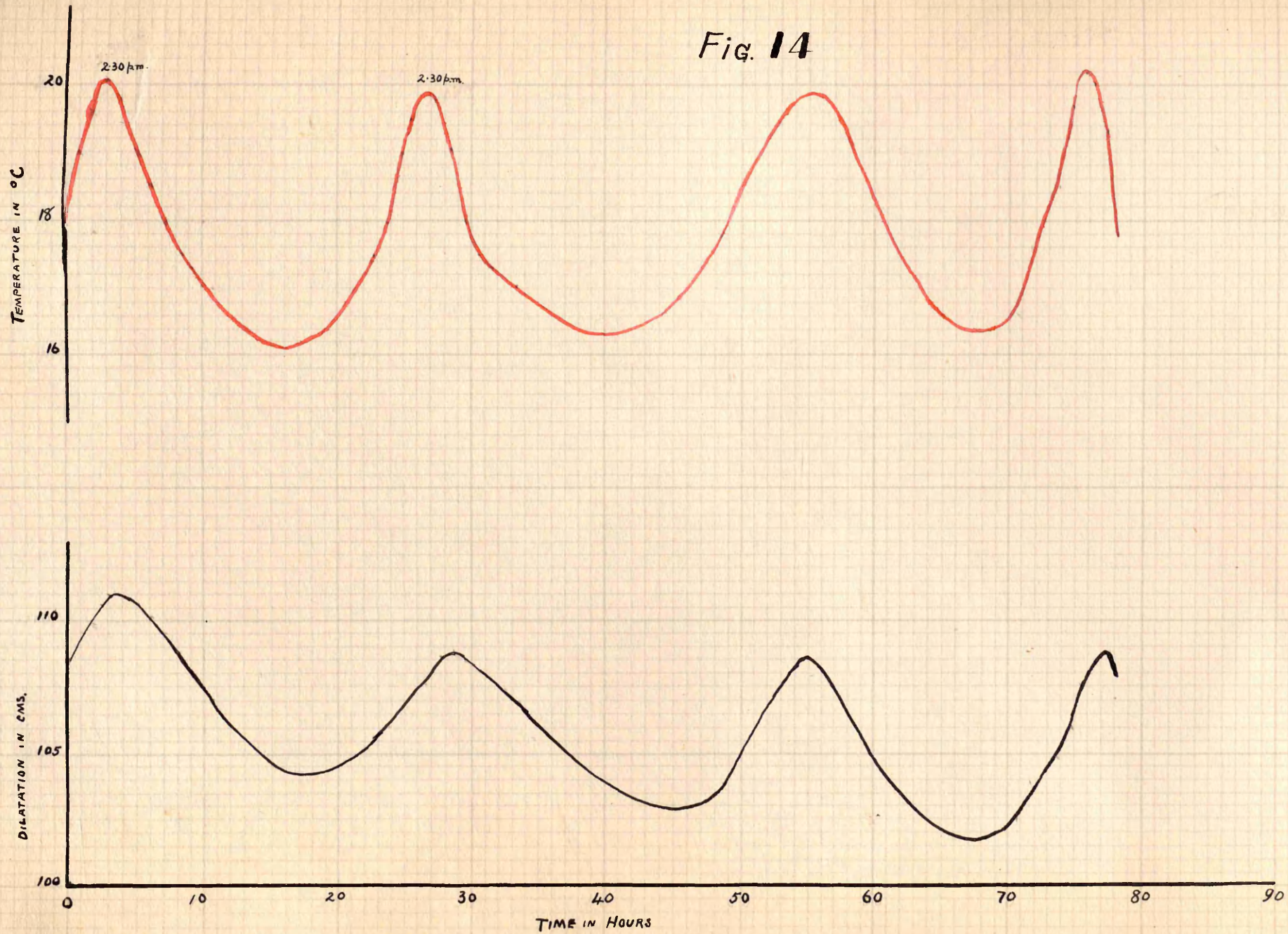
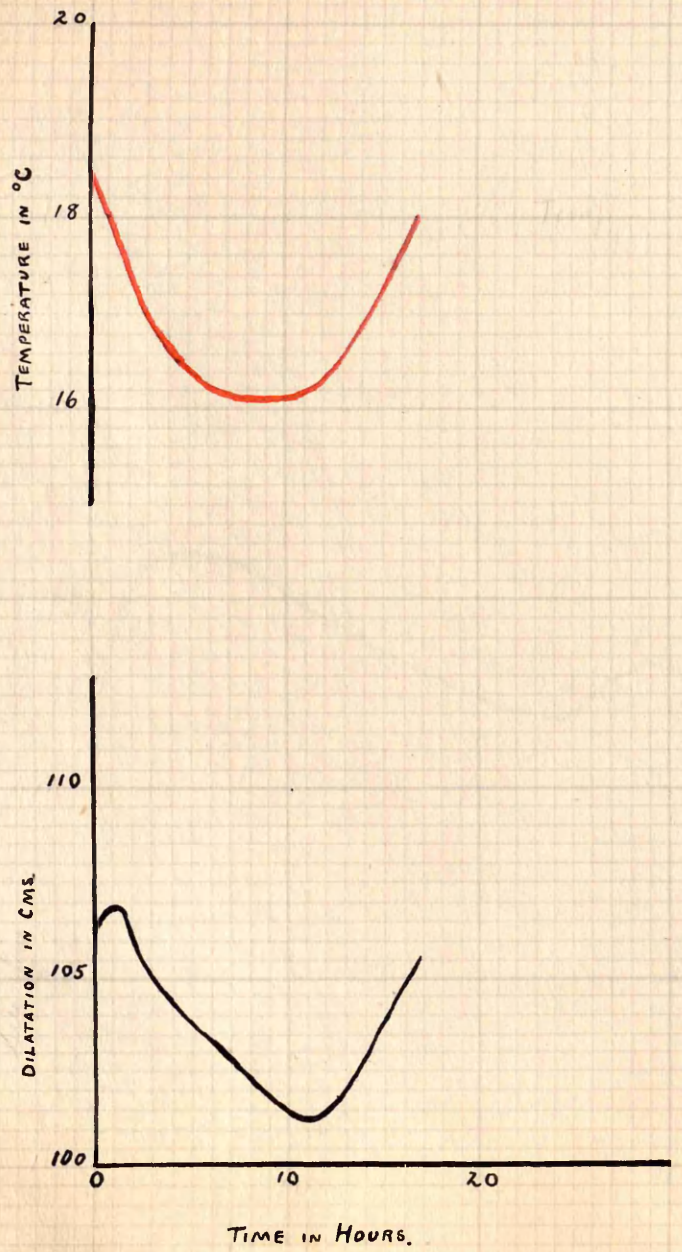
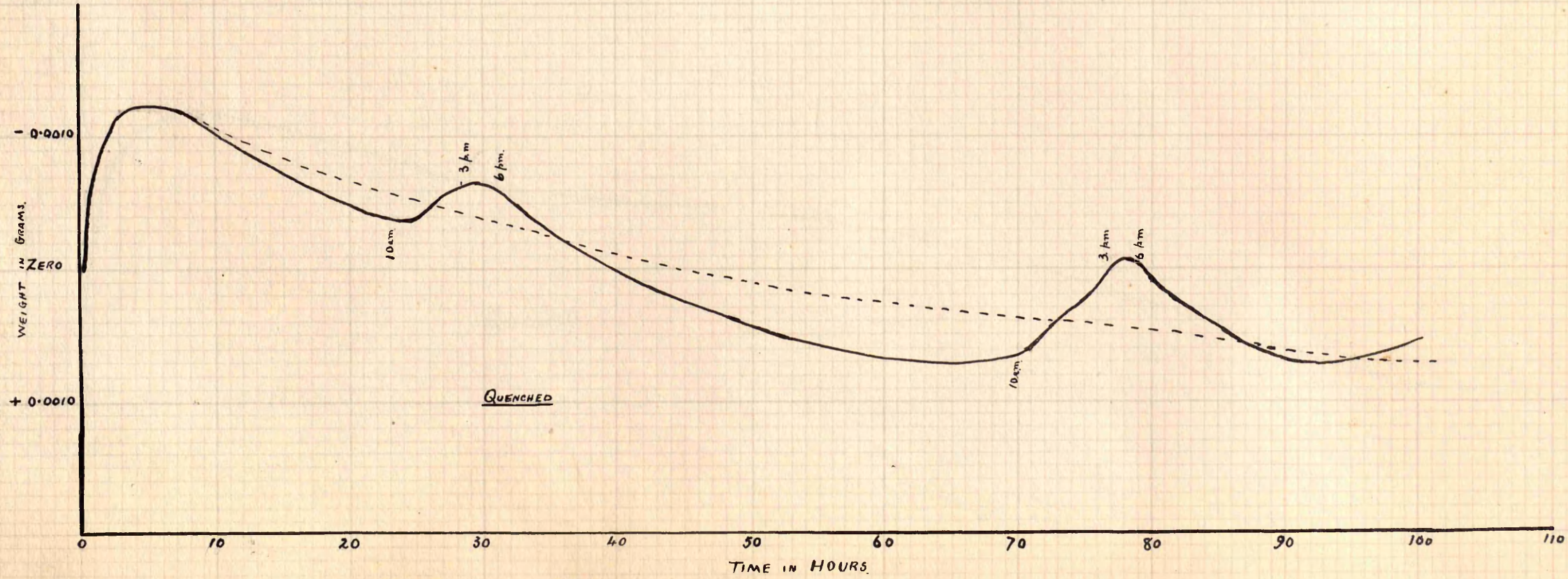

2·30 p.m.
2·30 p.m.
20
18
16
TEMPERATURE IN °C
110
105
100
DILATATION IN CMS.
0
10
20
30
40
50
60
70
80
90
TIME IN HOURS

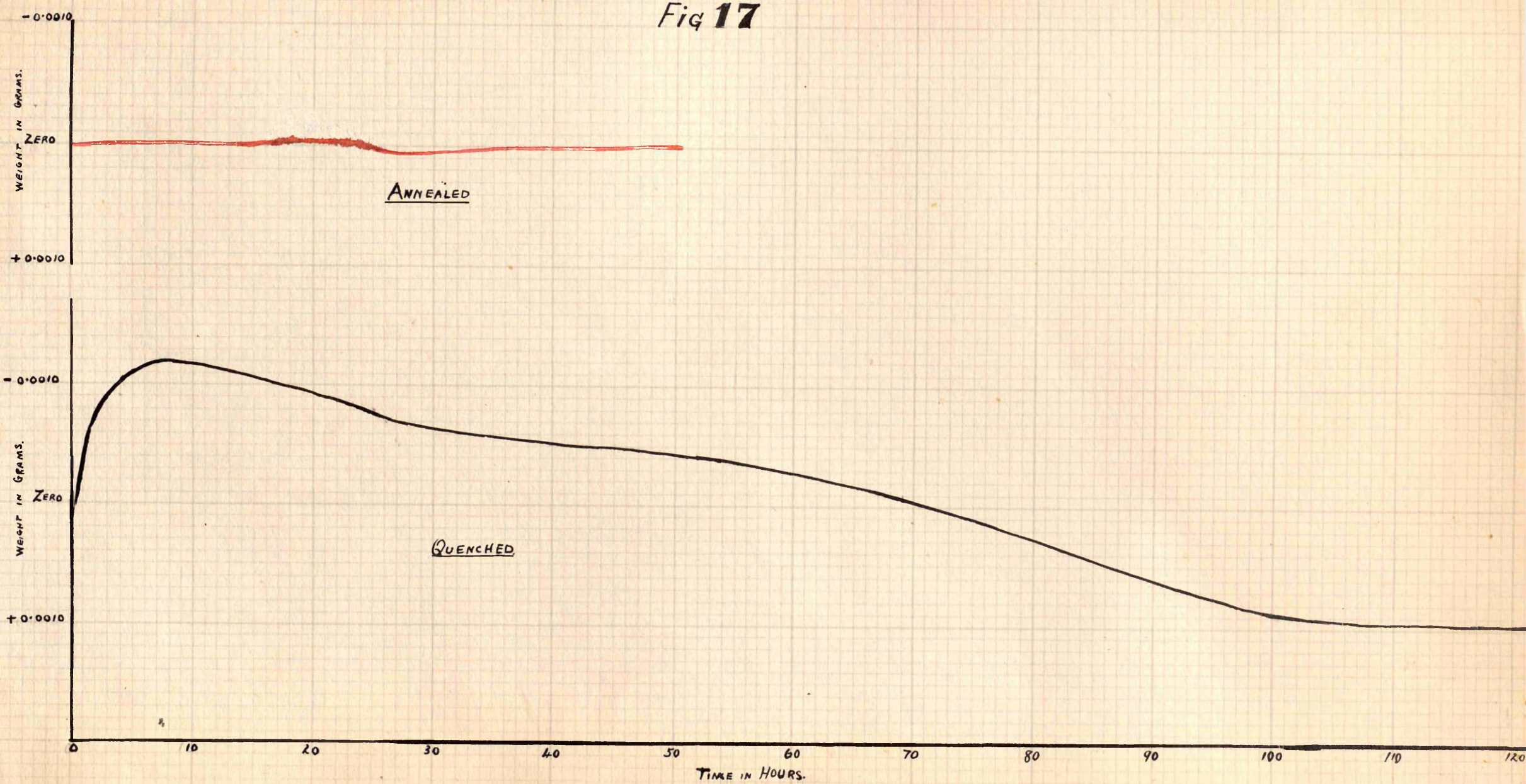
Fig. 15


20
18
16
TEMPERATURE IN °C
110
105
100
DILATATION IN CMS.
0
10
20
TIME IN HOURS.

# FIG 16


- 0·0010
WEIGHT IN GRAMS.
ZERO
+ 0·0010
10 cm.
3 hm
6 hm.
QUENCHED
10 cm.
3 hm
6 hm
0
10
20
30
40
50
60
70
80
90
100
110
TIME IN HOURS.

# Fig 17


- 0·0010
WEIGHT IN GRAMS.
ZERO
+ 0·0010
ANNEALED
- 0·0010
WEIGHT IN GRAMS.
ZERO
+ 0·0010
QUENCHED
0
10
20
30
40
50
60
70
80
90
100
110
120
TIME IN HOURS.

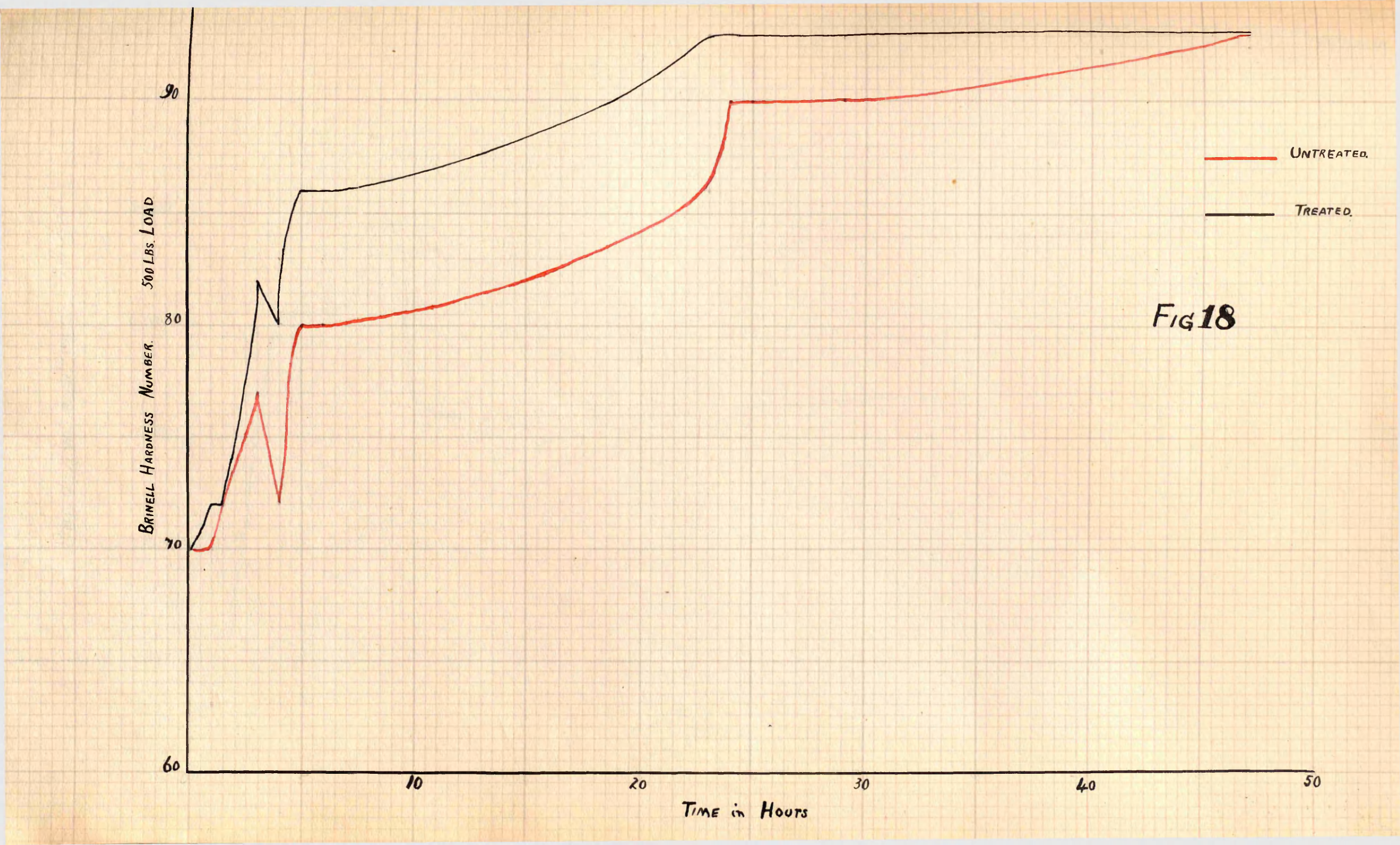
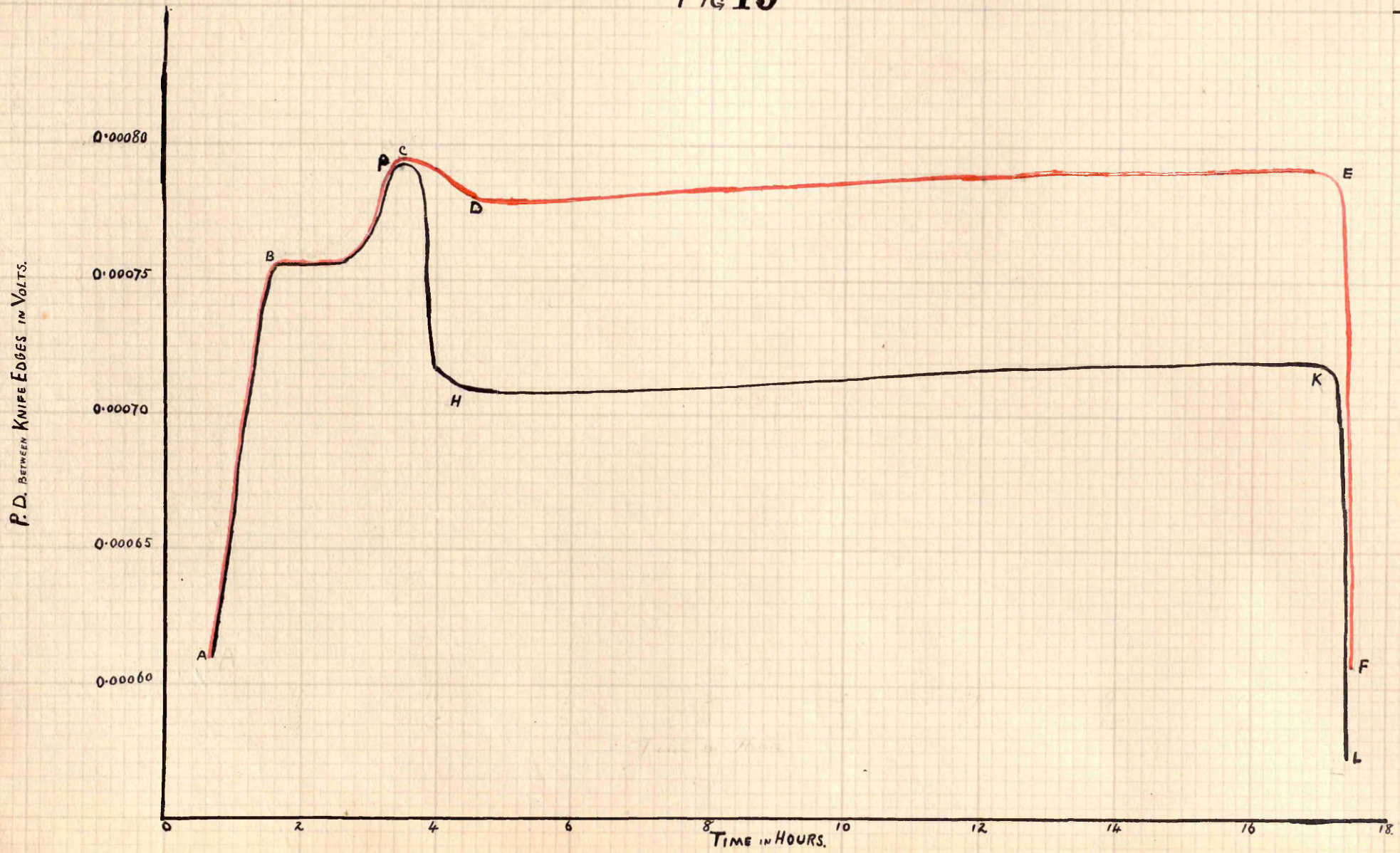

90
80
70
60
BRINELL HARDNESS NUMBER. 500 LBS. LOAD
10
20
30
40
50
TIME in HOURS
UNTREATED.
TREATED.

FIG 18

FIG 19


UNTREATED
TREATED
P.D. BETWEEN KNIFE EDGES IN VOLTS.
0·00080
0·00075
0·00070
0·00065
0·00060
A
B
P
C
D
E
F
H
K
L
0
2
4
6
8
10
12
14
16
18
TIME IN HOURS.